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Forty-Fourth Annual Meeting American Ceramic Society April 19-25, 1942

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THE AMERICAN CERAMIC SOCIETY

2525 North High Street **Columbus, Ohio**

THE JOURNAL

OF

THE AMERICAN CERAMIC SOCIETY

Vol. 25 February 1, 1942 No. 3

EFFECT OF BARIUM OXIDE AND ZINC OXIDE ON PROPERTIES OF SODA-DOLOMITE LIME-SILICA GLASS*

CONTRIBUTION OF THE GENERAL RESEARCH LABORATORY, OWENS-ILLINOIS GLASS COMPANY†

ABSTRACT

To a base glass containing 14% of sodium oxide, 12% of dolomite lime, and 74% of silica, barium oxide and zinc oxide, respectively, were systematically substituted for (*a*) Na_2O, (*b*) $CaO \cdot MgO$, and (*c*) SiO_2 in amounts of 1, 3, and 5%. The effects of these substitutions on such physical properties as liquidus temperature, viscosity, deformation temperature, density, fiber softening point, coefficient of expansion, and the resistance of the glasses to dilute acid and distilled water are presented.

I. Introduction

During the past several years, this laboratory has carried out a number of investigations of the effect of composition on several important physical and chemical properties of that type of glass commonly referred to as "soda-lime." Two of the largest series studied have been (*A*) the system Na_2O–$CaO \cdot MgO$–Al_2O_3–SiO_2 and (*B*) the system Na_2O–CaO–Al_2O_3–SiO_2. This paper describes the effect of the substitution of BaO and of ZnO for (*a*) SiO_2, (*b*) $CaO \cdot MgO$, and (*c*) Na_2O in one typical soda-dolomite lime-silica glass in the series referred to as the (*A*) series.

II. Chemical Composition and Preparation of the Glasses

The raw materials used in the preparation of the glasses were Ottawa sand, burned dolomite, Solvay soda ash, barium carbonate, zinc oxide, and ammonium sulfate. Ammonium sulfate in an amount sufficient to yield approximately 0.2% of SO_3 in the finished glass was used as a refining agent in the preparation of all of the glasses. The analyses of the raw materials which introduced small amounts of impurities into the glasses were as follows:

	Burned dolomite	Ottawa sand
SiO_2	0.6	99.7
R_2O_3	0.3	0.2
SO_3	0.6	
CaO	57.2	
MgO	40.1	
Ignition loss	1.2	

Approximately $4^1/_2$ lb. of each glass were melted in a large covered platinum crucible in a gas-fired furnace. The glasses were stirred several times during the initial melting period and were poured, crushed, and remelted with additional stirring. The total time of melting and remelting was approximately 20 hours at approximately 2600°F.

The actual chemical analyses as well as all measured properties of the barium oxide glasses may be found in Table I. Analyses and all measured properties of the zinc oxide glasses are shown in Table II. The first analysis shown in each of these tables, referred to in Table I as Ba-O and in Table II as Z-O, is the same, that is, the base glass is common to both series.

In making the substitutions, attempts were made to substitute both BaO and ZnO in steps of 1, 3, and 5% for (*a*) SiO_2, (*b*) $CaO \cdot MgO$, and (*c*) Na_2O. An examination of the analyses shows that, except for the substitution of ZnO for $CaO \cdot MgO$ and for Na_2O, the desired substitutions were obtained fairly closely. In the ZnO and $CaO \cdot MgO$ series, it is obvious that as the ZnO content was increased, progressively greater amounts of the material entered into the glasses at the expense of SiO_2 in addition to the amounts which were substituted for $CaO \cdot MgO$ and Na_2O, respectively. This condition was caused by poor estimations of the amount of ZnO which was expected to be volatilized during melting. Its actual effect on the measured

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941 (Glass Division). Received May 14, 1941.

†This work was a cooperative effort under the supervision of C. L. Babcock and W. B. Silverman. The following members of the research staff were responsible for the preparation of glasses, chemical analyses, and measurement of various properties: Paul Close, Frank R. Bacon, J. F. White, V. C. Rees, J. Miller, and R. C. Kennedy.

TABLE I

CHEMICAL ANALYSES AND PROPERTIES OF BARIUM OXIDE GLASSES TESTED*

	(1) Ba-0	(2) Ba-1S	(3) Ba-3S	(4) Ba-5S	(5) Ba-1D	(6) Ba-3D	(7) Ba-5D	(8) Ba-1N	(9) Ba-3N	(10) Ba-5N
SiO_2	73.6	72.7	70.7	69.1	73.7	73.7	73.5	73.4	73.5	73.5
R_2O_3	0.2	0.2	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2
CaO	7.1	7.2	7.1	7.0	6.5	5.3	4.2	7.1	7.1	7.2
MgO	4.9	4.9	4.9	4.8	4.5	3.6	2.9	5.0	4.9	5.0
Na_2O	13.9	13.7	13.9	13.8	13.9	13.8	13.9	12.8	11.1	8.9
SO_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
BaO		1.0	3.0	5.0	1.0	3.0	5.0	1.1	3.0	4.9
	99.9	99.9	99.9	100.0	99.9	99.8	99.9	99.8	100.0	99.9
Viscosity										
Log = 2	2667°F.	2669°F.	2579°F.	2597°F.	2683°F.	2696°F.	2701°F.	2670°F.	2727°F.	2856°F.
3	2208	2196	2136	2120	2208	2219	2217	2220	2251	2334
4	1906	1888	1846	1823	1897	1908	1897	1920	1940	2007
5	1692	1672	1643	1618	1679	1686	1670	1705	1722	1782
6	1531	1512	1492	1470	1519	1519	1499	1545	1564	1620
7	1407	1389	1375	1359	1396	1391	1366	1420	1438	1495
7.65	1342	1324	1314	1299	1330	1324	1296	1355	1373	1431
Liquidus temp. (°F.)	1840	1805	1760	1735	1850	1890	1965	1910	2075	2315
Coeff. of expansion ($\times 10^7$/°C.)	87	87	94	95	87	89	88	84	81	72
Deformation temp. (°F.)	1064	1070	1061	1049	1060	1047	1020	1083	1092	1115
Chemical duration (% of Na_2O) water	0.058	0.060	0.060	0.068	0.060	0.061	0.071	0.050	0.045	0.039
Chemical durability (% of Na_2O) acid	0.028	0.026	0.030	0.032	0.029	0.033	0.043	0.022	0.014	0.009
Density	2.4825	2.5025	2.5426	2.5902	2.4897	2.5035	2.5238	2.4960	2.5148	2.5412

* The tridymite phase occurs in each glass except in columns (3) and (4), in which the diopside phase occurs.

properties of the glasses, however, is probably within the experimental accuracy of the determinations.

III. Properties Measured and Methods of Determination

The following properties of the glasses were determined: (1) density, (2) liquidus temperature, (3) coefficient of expansion, (4) deformation temperature,* (5) viscosity, (*a*) fiber softening point and (*b*) high-temperature viscosity, (6) resistance to dilute acid, and (7) resistance to distilled water.

(1) Density

The weights of the samples used for density determinations varied between 4 and 6 grams. They were prepared by remelting and fining, in small platinum boats, glass which had been crushed to pass a 100-mesh sieve. All samples were annealed together from 1100°F. to room temperature so that each was subjected to the same thermal treatment.

The density determinations were made by the displacement method of weighing the sample (*a*) in air and (*b*) suspended in distilled water which had been previously boiled under a vacuum to expel carbon dioxide. The temperature of the distilled water at the time the weighing was made was measured and ranged between 72° and 75°F. The accuracy of the determinations is considered to be of the order of ±0.0003.

(2) Liquidus Temperature

Liquidus temperature determinations were made by the so-called temperature-gradient method, which has been described by Silverman.[1]

(3) and (4) Coefficient of Expansion and Deformation Temperature

The linear coefficients of thermal expansion were determined by the interferometer method, which has been described in several papers.[2] The description of the furnace used and details of the exact method employed have been described by Silverman.[3]

The samples were in the shape of pyramids approximately 0.20 in. high. The heating schedule of the furnace was 3°C. per minute. Temperature measurements were made with a platinum-platinum rhodium thermocouple and a Leeds & Northrup semiprecision

* The term, "deformation temperature," is used here to designate the temperature at which glasses cease to expand in the interferometer method for determining the dilation characteristics of a glass. The term is employed to avoid the use of "softening point," which was defined by Littleton (see footnote 4 of this paper) as the temperature at which a glass fiber, 1 mm. in diameter and 22.9 cm. long, elongates at the rate of 1 mm. per minute when it is heated at the rate of 5°C. per minute. The term, "deformation point," adequately describes the phenomenon associated with this temperature in the annealing process because glass objects held in the region near this temperature for a sufficiently long time become "chain-marked."

[1] W. B. Silverman, "Effect of Alumina on the Devitrification of Soda-Lime-Silica Glasses," *Jour. Amer. Ceram. Soc.*, **22** [11] 378–84 (1939).

[2] G. E. Merritt, "Interference Method of Measuring Thermal Expansion," *Bur. Stand. Jour. Research*, **10** [1] 59–76 (1933); R.P. 515; *Ceram. Abs.*, **12** [3] 129 (1933).

[3] W. B. Silverman, "Effect of Alumina on Expansion and Deformation Temperatures of Soda-Lime-Silica Glasses," *Jour. Soc. Glass Tech.*, **24** [102] 59–72T (1940); *Ceram. Abs.*, **19** [10] 232(1940).

TABLE II

CHEMICAL ANALYSES AND MEASURED PROPERTIES OF ZINC OXIDE GLASSES TESTED*

	(1) Zn-O	(2) Zn-1S	(3) Zn-3S	(4) Zn-5S	(5) Zn-1D	(6) Zn-3D	(7) Zn-5D	(8) Zn-1N	(9) Zn-3N	(10) Zn-5N
SiO_2	73.6	72.6	70.4	68.2	73.5	73.4	73.2	73.6	73.5	73.3
R_2O_3	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
CaO	7.1	7.0	7.1	7.1	6.5	5.3	4.1	7.1	7.1	7.1
MgO	4.9	4.9	4.9	4.9	4.5	3.8	2.9	4.9	4.9	4.9
Na_2O	13.9	13.8	13.8	13.8	13.9	13.9	13.9	12.9	10.9	9.0
SO_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
ZnO		1.1	3.3	5.4	1.2	3.3	5.4	1.2	3.3	5.4
	99.9	99.8	99.9	99.9	99.9	100.0	99.8	100.0	100.0	100.0
Viscosity										
Log = 2	2667°F.	2640°F.	2600°F.	2520°F.	2710°F.	2720°F.	2740°F.	2710°F.	2765°F.	2810°F.
3	2208	2185	2155	2110	2215	2220	2240	2230	2275	2320
4	1906	1885	1865	1840	1900	1900	1915	1920	1965	2000
5	1692	1675	1655	1643	1680	1682	1690	1707	1745	1780
6	1531	1520	1504	1495	1520	1523	1530	1546	1580	1615
7	1407	1400	1385	1380	1400	1400	1405	1425	1455	1492
7.65	1342	1335	1323	1317	1335	1337	1335	1360	1390	1425
Liquidus temp. (°F.)	1840	1790	1825	1890	1845	1855	1870	1860	2100	2265
Coeff. of expansion ($\times 10^7$/°C.)	87	88	90	91	86	87	89	85	80	71
Deformation temp. (°F.)	1064	1066	1071	1063	1064	1064	1053	1080	1116	1125
Chemical durability (% of Na_2O) water	0.058	0.047	0.028	0.019	0.044	0.028	0.024	0.037	0.018	0.010
Chemical durability (% of Na_2O) acid	0.028	0.027	0.029	0.030	0.028	0.025	0.034	0.020	0.011	0.008
Density	2.4825	2.5067	2.5464	2.5846	2.4900	2.5046	2.5188	2.4958	2.5148	2.5390

* The tridymite phase occurs in each glass except in columns (2), (3), and (4), in which the diopside phase occurs.

potentiometer. The hot junction of the thermocouple was fixed at a point about $1/16$ in. below the bottom plate of the interferometer. The light source was obtained from a filtered mercury spectrum with a wave length of 5461 a.u.

The coefficients of expansion were computed from the usual equation,

$$\alpha = 1/L_0 \, \Delta L/\Delta t.$$

Δl = change of length.
L_0 = length at room temp.
Δt = (170°C. − 80°C.) = 90°C.

The accuracy of the method of measurement is computed to be something less than 2%.

The accuracy of the deformation temperature has been found on numerous occasions to be about 5°F.

(5) Viscosity

(*A*) *Fiber Softening Point:* The method used to determinate the fiber softening point has been described by Littleton.[4]

(*B*) *High-Temperature Viscosity:* The high-temperature viscosities were measured by using the falling-sphere method, described by Hunter,[5] at four temperatures for each glass, ranging from approximately 2450° F. down to the liquidus temperature of the glass. From these four experimental values and from the fiber softening point (shown by Lillie[6] to correspond to a temperature at which the log viscosity of the glass is 7.65), the complete viscosity curves were calculated by an empirical equation described by Fulcher.[7]

(6) Resistance to Dilute Acid

The resistance of glasses to dilute acidic solutions was determined by the so-called American Ceramic Society method No. 1.[8]

(7) Resistance to Distilled Water

The resistance of the glasses to distilled water was determined by a modification of The American Ceramic Society method No. 1, in which previously boiled distilled water was substituted for $N/50$ H_2SO_4. At the end of the 4-hour period at 90°C., the flask containing the sample was removed from the water bath and cooled quickly to room temperature. Exactly 40 cc. of the fluid contents were removed by a pipette and transferred to a clean flask. A small measured amount of $N/50$ H_2SO_4, slightly in excess of that required to reach a methyl red end point, was added to the solution, which was then brought quickly to boil to expel carbon dioxide and back titrated to a methyl red end point with $N/50$ NaOH solution. The results are expressed in percentage of Na_2O leached from the sample.

[4] J. T. Littleton, Jr., "Method for Measuring Softening Temperature of Glasses," *Jour. Amer. Ceram. Soc.*, 10 [4] 259–64 (1927).

[5] R. G. Hunter, "Application of Stokes' Law in the Determination of Absolute Viscosity of Glass," *ibid.*, 17 [5] 121–27 (1934).

[6] H. R. Lillie, "Viscosity of Glass Between Strain Point and Melting Temperature," *ibid.*, 14 [7] 502–11 (1931).

[7] G. S. Fulcher, "Analysis of Recent Measurements of Viscosity of Glasses, II," *ibid.*, 8 [12] 789–94 (1925).

[8] Report of Committee on Chemical Durability of Glass, *Bull. Amer. Ceram. Soc.*, 14 [5] 181–84 (1935).

IV. Discussion of Results

All of the measured data obtained on the nineteen glasses are shown in Tables I and II. The effects of the substitutions on the various properties may be more readily observed by examination of Figs. 1 to 19.

(1) Density

(*a*) An examination of Fig. 1, showing the effect of the substitution of barium oxide on density, indicates that, per cent for per cent, the substitution of BaO for SiO_2, Na_2O, or CaO·MgO results in an increase in density. The amount of increase per percentage of substitution for these oxides is approximately 0.021, 0.011, and 0.008, respectively.

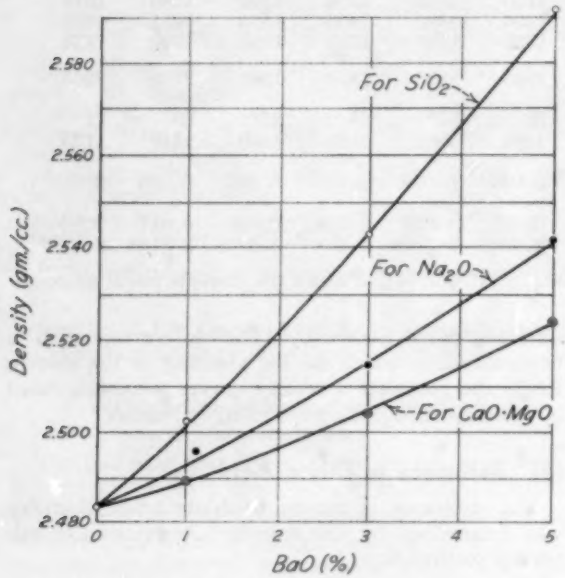

FIG. 1.—Effect of BaO substitutions on density.

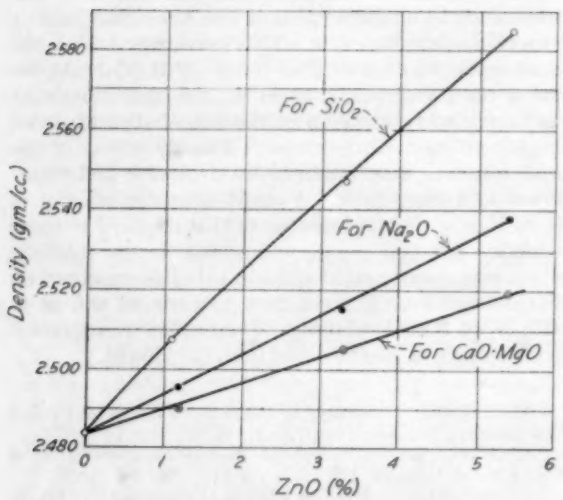

FIG. 2.—Effect of ZnO substitutions on density.

(*b*) The substitution of ZnO for the constituent oxides of the base glass results in an increase in density in every case. The amount of increase per percentage of substitution is approximately 0.19% for SiO_2, 0.010% for Na_2O, and 0.006 % for CaO·MgO.

It is obvious from Figs. 1 and 2 that the effect of adding either BaO or ZnO to the glass sample is to increase the density, and the effect of the BaO addition is slightly greater than that of ZnO.

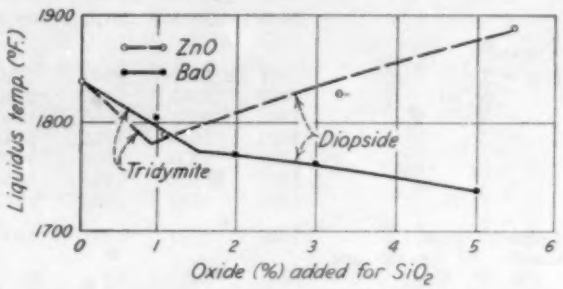

FIG. 3.—Effect of replacement of SiO_2 on liquidus temperatures.

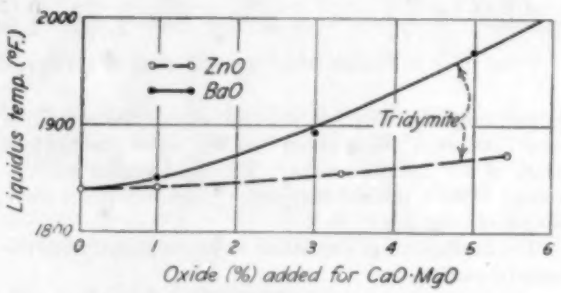

FIG. 4.—Effect of replacement of CaO·MgO on liquidus temperatures.

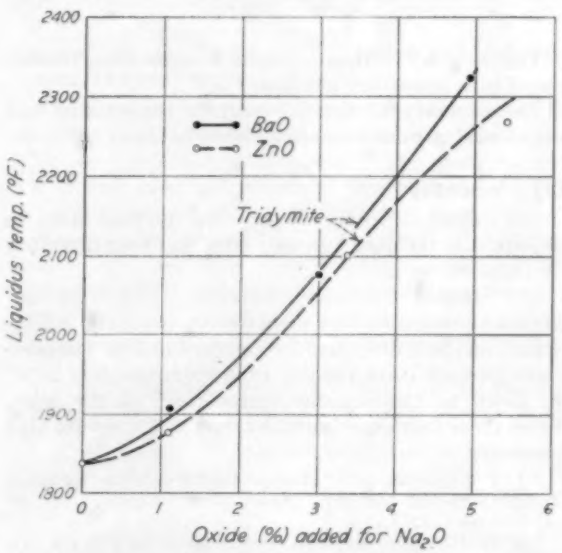

FIG. 5.—Effect of replacement of Na_2O on liquidus temperatures.

(2) Liquidus Temperature

Figures 3, 4, and 5 show the effect on the liquidus temperature of the substitution of (*a*) BaO and (*b*) ZnO for SiO_2, $CaO \cdot MgO$, and Na_2O, respectively.

Figure 3 shows that the substitution of BaO for SiO_2 up to amounts as great as 5% results in a continual decrease of liquidus temperature. The primary phase changes from tridymite to diopside at about $1^1/_2$% of BaO so substituted. The substitution of ZnO for SiO_2 results in an initial decrease of liquidus, the minimum being obtained at about 1.0% of ZnO. Further substitution causes an increase in the liquidus temperature and results in a change of the primary phase from tridymite to diopside.

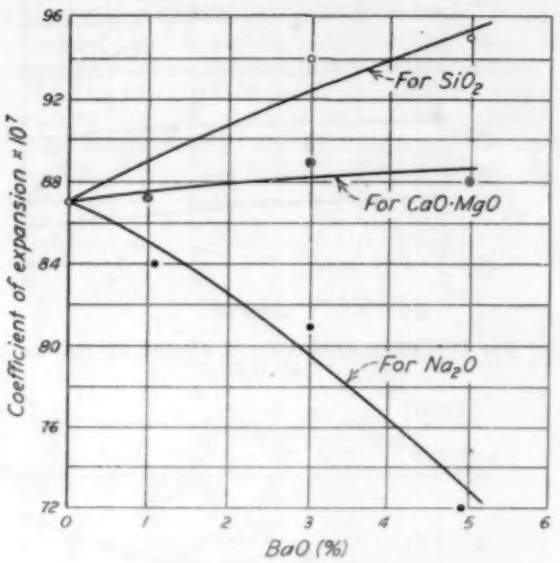

FIG. 6.—Effect of BaO substitutions on coefficient of expansion.

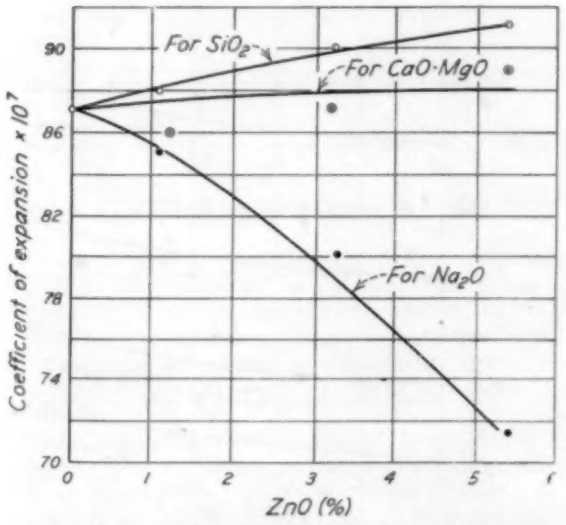

FIG. 7.—Effect of ZnO substitutions on coefficient of expansion.

Figure 4 shows that substitution of either BaO or ZnO for $CaO \cdot MgO$ results in an increase in the liquidus temperature; BaO increases the liquidus at a greater rate than ZnO; and tridymite remains as the primary phase in both cases.

When BaO or ZnO is substituted for Na_2O, a rapid and great increase occurs in the liquidus temperature (see Fig. 5).

(3) Coefficient of Expansion

The effects of substituting BaO for the various constituent oxides on the coefficient of expansion of the glass are shown in Fig. 6. An examination of this figure indicates that BaO substitution for silica increases the expansion coefficient appreciably, that substitution for $CaO \cdot MgO$ results only in a slight increase of the coefficient, and that a considerable decrease in the expansion factor occurs when it is substituted for Na_2O. It would also appear from examination of Fig. 6 that the effect of BaO on the expansion of a soda-

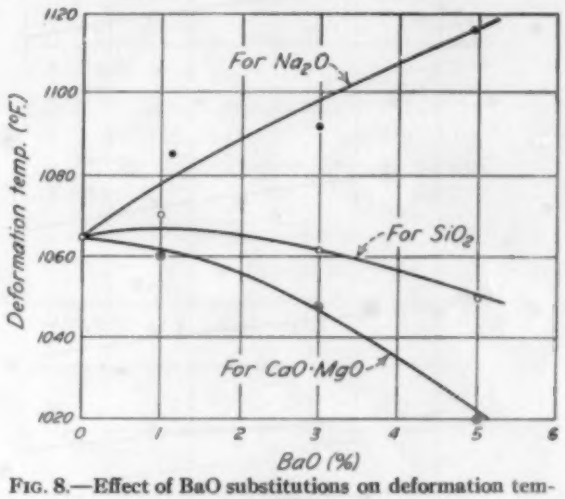

FIG. 8.—Effect of BaO substitutions on deformation temperatures.

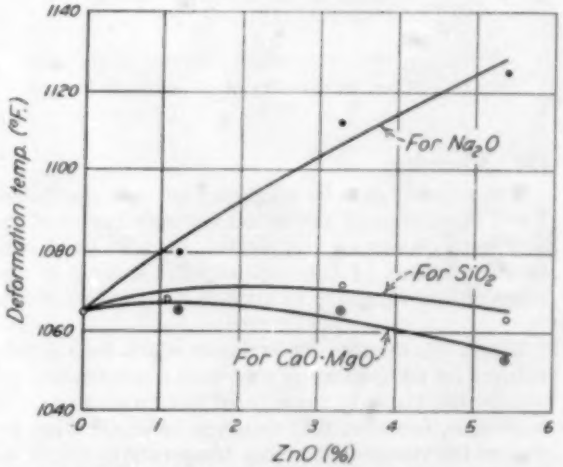

FIG. 9.—Effect of ZnO substitutions on deformation temperatures.

dolomite lime glass is about as great in magnitude as is that of CaO·MgO.

Figure 7 shows that, except when ZnO is substituted for SiO_2, its action on the coefficient of expansion is similar to that of BaO; ZnO appears to raise the expansion considerably less than BaO when the oxides are substituted for SiO_2.

(4) Deformation Temperature

Figures 8 and 9 show the effects of the substitutions on deformation temperature. The data indicate (1) that the substitution of either oxide for Na_2O increases the deformation temperature; (2) that when a substitution is made at the expense of SiO_2, ZnO has little effect but that BaO appreciably lowers the temperature; and (3) that the substitution of BaO for CaO·MgO lowers the deformation temperature considerably, whereas it is lowered only slightly when ZnO is substituted in the same manner.

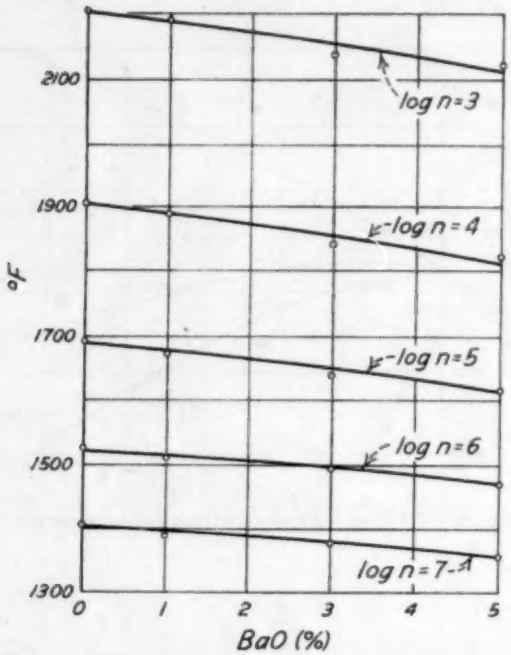

FIG. 10.—Effect on viscosity of substituting BaO for SiO_2.

(5) Viscosity

The viscosity data for all glasses are shown in Tables I and II. Although the actual viscosity curves of the individual glasses are not plotted, Figs. 10 to 15 indicate the effects of the various substitutions on the temperatures necessary to attain log viscosities of 3 to 7.

Figure 10, showing the series in which BaO is substituted for SiO_2, indicates that such a substitution decreases the viscosity throughout the range given. It is obvious, however, that this type of substitution decreases the viscosity at higher temperatures (2100° to 2200°F.) to a greater extent than at low temperatures (1400° to 1500°F.).

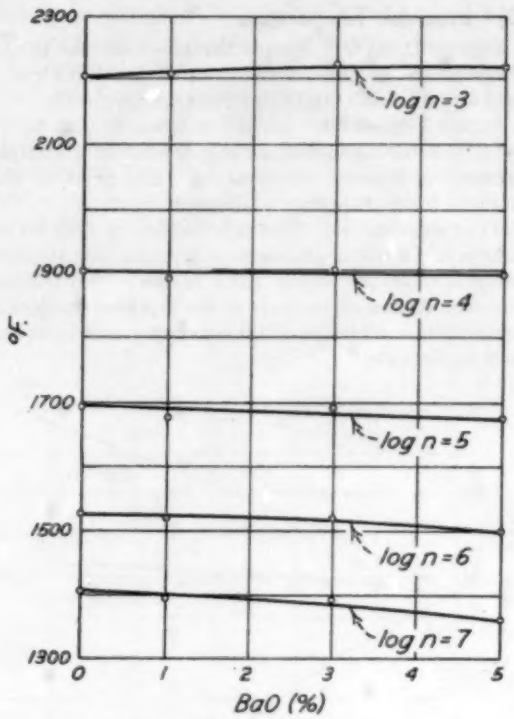

FIG. 11.—Effect on viscosity of substituting BaO for CaO·MgO.

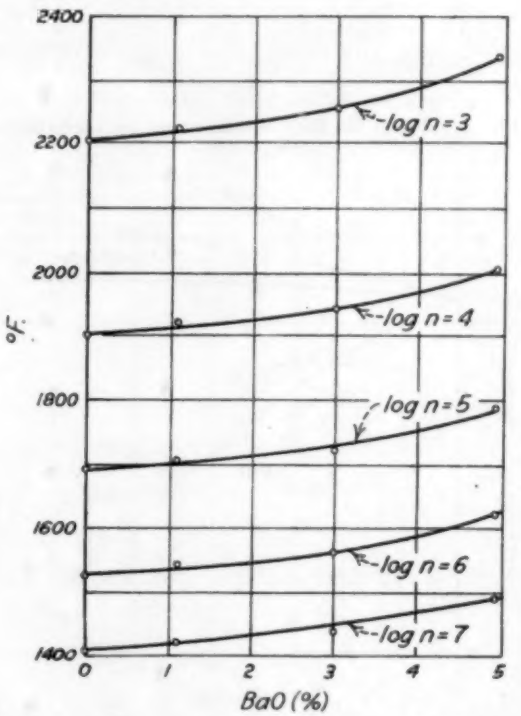

FIG. 12.—Effect on viscosity of substituting BaO for Na_2O.

Figure 11, in which the effect on viscosity of substituting BaO for CaO·MgO is plotted, shows that the substitution causes a slight increase in viscosity at high temperatures, such as 2200°F., and that there is a considerable decrease in viscosity at low temperatures (1400° to 1500°F.). The net effect of the substitution, therefore, is a lengthening of the working range or a decrease in the setting rate.

Figure 12, showing the effect of the substitution of BaO for Na_2O on viscosity, indicates that the lines plotted to show necessary temperatures to attain any given log viscosity have a definite curvature and that the low-temperature viscosities are increased almost as much as are those at high temperatures.

Figure 13, which shows the substitution of ZnO for SiO_2, indicates that a decrease in viscosity occurs throughout the temperature range studied. At high temperatures, in the range of 2200°F., this substitution is about as effective in lowering viscosity as is that of BaO for SiO_2; at low temperatures (1400° to 1500° F.), the substitution of ZnO for SiO_2 lowers the viscosity considerably less than when BaO is substituted for SiO_2.

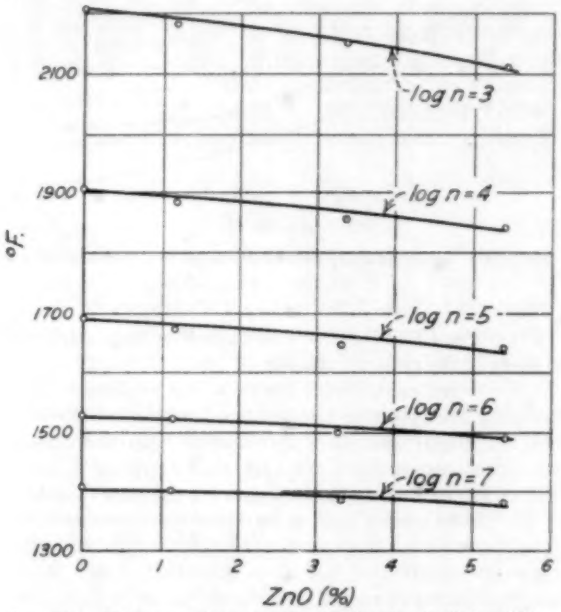

FIG. 13.—Effect on viscosity of substituting ZnO for SiO_2.

Figure 14 indicates that when ZnO is substituted for CaO·MgO the viscosities in the temperature range around 2200°F. are increased slightly, whereas at 1400° to 1500°F. they remain substantially constant. The net effect of the substitution would therefore appear to be a slight increase in working range or a decrease in setting rate.

Figure 15 indicates that the effect of the substitution of ZnO for Na_2O is to increase the viscosity considerably throughout the temperature range studied. A comparison of this figure with Fig. 12 indicates that when either ZnO or BaO is substituted for Na_2O the effects on viscosity are similar.

(6) Resistance to Dilute Acid

The effects of the substitution of BaO and ZnO on the so-called acid durability of a glass are shown in Figs. 16 and 17, respectively. Figure 16 indicates that substitution of BaO for SiO_2 results initially in a slight

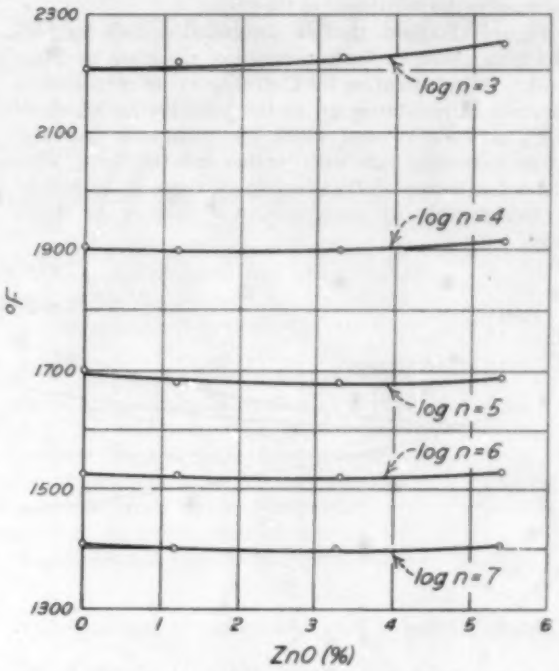

FIG. 14.—Effect on viscosity of substituting ZnO for CaO·MgO.

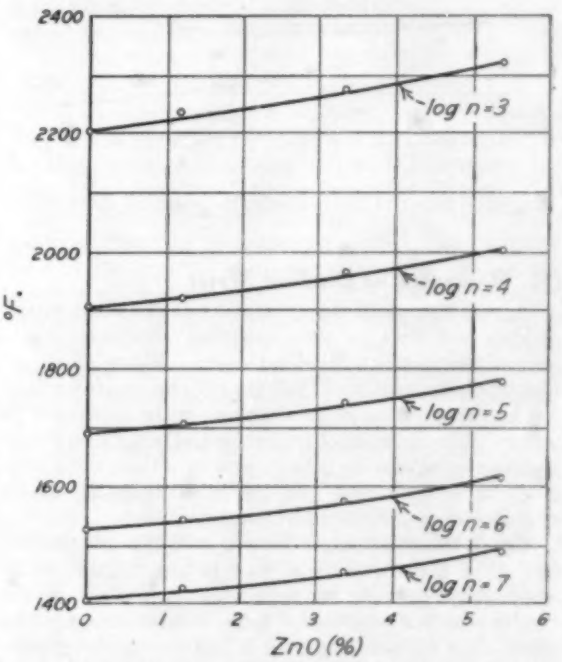

FIG. 15.—Effect on viscosity of substituting ZnO for Na_2O.

increase and finally in a slight decrease in the resistance of the glass to dilute acid. With the substitution of BaO for CaO·MgO, there is an appreciable decrease in its resistance to dilute acid, and the rate of decrease increases as the amount of BaO substituted is increased. The substitution of BaO for Na_2O causes a substantial increase in the resistance of the glass.

Figure 17 shows that substitution of ZnO for SiO_2 has little effect on the resistance of the glass to dilute acid. Its substitution for CaO·MgO results in a slight increase in resistance up to the substitution of about 3.0% of ZnO, beyond which the resistance decreases at an increasing rate with further substitution. With the substitution of ZnO for Na_2O, there is, of course, a considerable improvement in resistance to dilute acid.

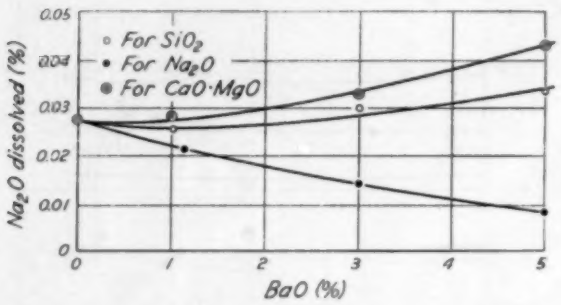

FIG. 16.—Effect of BaO substitution on acid durability.

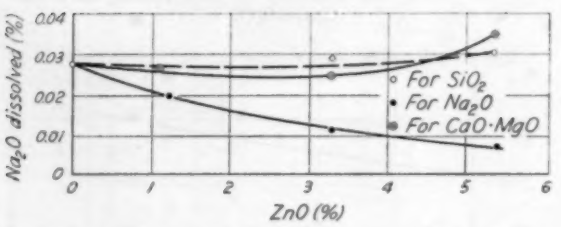

FIG. 17.—Effect of ZnO substitution on acid durability.

(7) Resistance to Distilled Water

Figures 18 and 19 show the effect of the substitution of BaO and ZnO for the constituent oxides on resistance of the glasses to distilled water. Figure 18 shows that the substitution of BaO for SiO_2 up to amounts of 5.0% effects only a slight decrease in the resistance to water. The same substitution for CaO·MgO decreases the resistance at a slightly greater rate than when BaO is substituted for SiO_2, and the substitution for Na_2O, of course, increases the resistance.

Figure 19, which shows the effect of the substitution of ZnO on the resistance of glass to water, indicates an appreciable increase in resistance, regardless of the constituent for which the ZnO is substituted. The effect of its substitution for Na_2O is slightly greater than that for either SiO_2 or CaO·MgO. A considerable increase in resistance is obtained nevertheless by substituting ZnO for either of the latter two constituents.

V. Conclusions

Seven chief conclusions may be drawn from the data presented, which are applicable only to the substitution of BaO or ZnO in the base glass described.

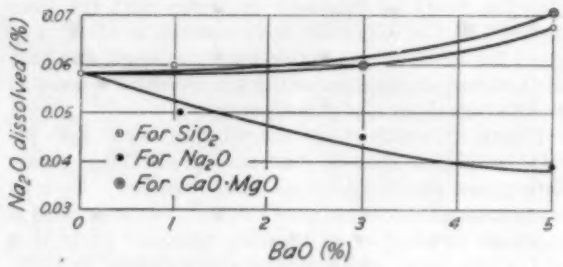

FIG. 18.—Effect of BaO substitution on water durability.

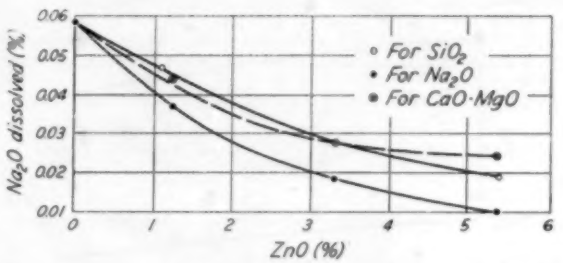

FIG. 19.—Effect of ZnO substitution on water durability.

(1) The effects of the two oxides on increasing the density of the glass are similar.

(2) When substituted for SiO_2, BaO is beneficial in lowering the liquidus temperature, whereas ZnO is at first beneficial and then detrimental. In the case of the substitution for CaO·MgO, ZnO causes a much less rapid rise in liquidus temperature than does BaO.

(3) Both oxides have approximately the same effect on the coefficient of expansion of the glass except when they are substituted for silica, in which case the expansion factor is raised considerably less by ZnO than by BaO.

(4) The substitution of BaO for SiO_2 or CaO·MgO results in an appreciable lowering of the deformation temperature or the upper annealing range; when ZnO is similarly substituted, the lowering of the deformation temperature is onsiderably less.

(5) At relatively high temperatures (2100° to 2200°F), both BaO and ZnO have about the same effect on viscosity as does dolomite lime. When substituted for CaO·MgO at low temperatures (1400° to 1500°F.), BaO decreases the viscosity and the ZnO substitution has little effect. The net result, therefore, is that when BaO is substituted for CaO·MgO the setting rate is decreased to a greater extent than when ZnO is substituted in the same manner.

(6) No benefits in the resistance of the glass to dilute acid are obtained by substituting either BaO or ZnO for SiO_2 or for $CaO \cdot MgO$.

(7) The substitution of BaO for either SiO_2 or $CaO \cdot MgO$ slightly decreases the resistance of the glass to distilled water, and the substitution of ZnO for the same constituents appreciably increases the resistance of the glass to this type of solution.

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ANALYSIS OF GASES DISSOLVED IN GLASS AND GASES PRESENT IN SEEDS*

By Hugh A. Shadduck and Arthur Van Zee

Abstract

A method of analysis for gases dissolved in glass has been developed which gives more reproducible results than those previously reported. The problem of the volatilization of alkali from the sample during the course of analysis appears to have been satisfactorily solved through the use of an auxiliary furnace. A number of commercial glasses have been analyzed for dissolved gases. Water vapor, sulfur dioxide, and oxygen are the principal gases found in flint glass. Water vapor seems to be the principal constituent of the gases found in amber glass.

A method for the analysis of gases present in seeds in glass has been developed which gives fairly satisfactory quantitative results on samples containing more than 1 cu. mm. of gas. The results obtained on samples containing less than 1 cu. mm. of gas are qualitative only. The procedure consists (1) in the determination of the temperatures at which gases present in the seeds undergo a change of state and (2) in the microchemical analysis of these same gases. Seeds have been found that contained entrapped air, sulfur dioxide, and also carbon dioxide. Some seeds, especially those in amber glass, appear to be vacuum seeds, and these frequently contain a deposit on the inside which has been identified as a sulfite or a sulfate.

Part I: Analysis of Gases in Glass

I. Introduction

According to Morey,[1] the first analysis of gases dissolved in glass was carried out by E. S. Shepherd and reported in an article by Allen and Zies.[2] A few papers have appeared since then on the extraction of gases dissolved in glass by means of heating the glass in a vacuum. The most recent of these papers are by Salmang and Becker,[3] Dalton,[4] and Hahner, Voigt, and Finn[5]; bibliographies on the subject appear in the book by Jebsen-Marwedel[6] and in the article by Weyl and Pincus.[7]

After some study, the following procedure was used for the extraction analysis of gases dissolved in glasses made by this company. The procedure follows to some extent that outlined by Dalton.[4]

II. Apparatus

The furnace assembly is shown in Fig. 1. Power is supplied to the main furnace by a transformer and an induction voltage regulator and to the auxiliary furnace (to be described later) from a 2-kva. Variac. The current enters the shell through copper leads sealed vacuum tight by Housekeeper seals. The temperature of the crucible is measured with an optical pyrometer through a flat glass window directly above the crucible. Radiation through this window is reflected into the pyrometer with a 45° mirror. The pyrometer was calibrated in place against a thermocouple in the crucible, thus eliminating the error due to absorption by the window and mirror. The bottom of the crucible is heated with a 0.075-in. diameter tantalum resistance wire furnace, known as the main furnace, im-

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Glass Division). Received June 1, 1941; revised paper received August 18, 1941.

[1] G. W. Morey, Properties of Glass, p. 97. Reinhold Publishing Corp., New York, N. Y., 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48 (1939).

[2] E. T. Allen and E. G. Zies, "Contribution to Methods of Glass Analysis with Special Reference to Boric Acid and Two Oxides of Arsenic," *Jour. Amer. Ceram. Soc.*, **1** [11] 739–86 (1918).

[3] H. Salmang and Alfred Becker, "Gases in Glass, I–III," *Glastech. Ber.*, **5** [11] 520–37 (1927); **6** [11] 625–34 (1928); **7** [6] 241–44 (1929); *Ceram. Abs.*, **7** [10] 672 (1928); **8** [9] 643 (1929); **9** [4] 267 (1930); English translation of Part II in *Jour. Soc. Glass Tech.*, **13**, 98–111T (1929).

[4] (*a*) R. H. Dalton, "Gases in Glass," *Jour. Amer. Ceram. Soc.*, **16** [9] 425–32 (1933).

(*b*) R. H. Dalton, "Extraction and Analysis of Gases from Glass," *Jour. Amer. Chem. Soc.*, **57** [11] 2150–53 (1935); *Ceram. Abs.*, **15** [9] 270 (1936).

[5] Clarence Hahner, G. Q. Voigt, and A. N. Finn, "Gases in Some Optical and Other Glasses," *Jour. Research Nat. Bur. Standards*, **19** [1] 95–103 (1937); R.P. 1014; *Ceram. Abs.*, **16** [9] 271 (1937).

[6] Hans Jebsen-Marwedel, Glastechnische Fabrikationsfehler (Technology of Defects in Glass Manufacture), pp. 58–99. Julius Springer, Berlin, 1936. 295 pp.; *Ceram. Abs.*, **16** [1] 16–17 (1937).

[7] W. A. Weyl and A. G. Pincus, "Role of Gases in Glass: I, Oxygen," *Glass Ind.*, **19** [7] 255–58; "II, Carbon Dioxide Evolution and Method of Following Reactions in Batch," *ibid.*, [9] 347–49; "III, Water," *ibid.*, [11] 417–19; "IV, Miscellaneous Gases," *ibid.*, [12] 455–56 (1938); *Ceram. Abs.*, **18** [5] 125–26 (1939).

bedded in fused alumina cement. These main furnaces can be conveniently made by winding tantalum wire on a lathe and sliding the coil on to a wooden core, such as a thermometer case wrapped with paper, for easy removal. The coarse cement† is mixed with water and is applied with a spatula.

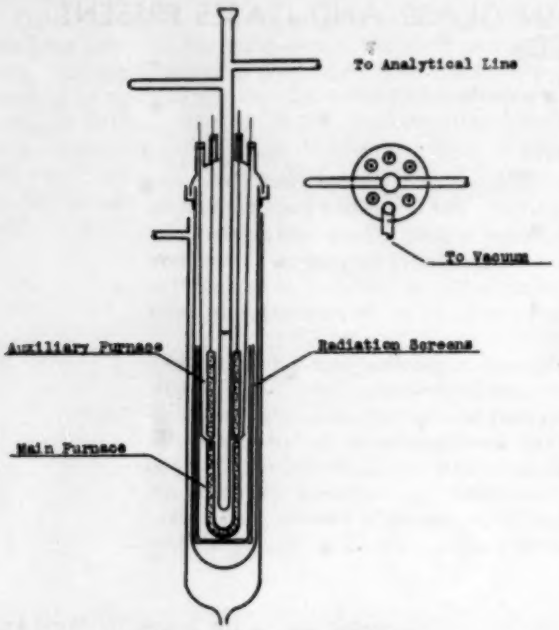

FIG. 1.—Furnace assembly.

The Bureau of Standards' paper[5] states ". . . the chief source of uncertainty has been the magnitude of the errors introduced by the absorption of gases by the alkaline materials that are volatilized from the molten glass." This difficulty was also noted by Salmang and Becker[3] and by Dalton.[4] The alkaline deposit absorbs such gases as carbon dioxide, sulfur dioxide and water vapor as they come from the glass. The writers believe that this difficulty has been overcome by using a relatively long crucible and placing an auxiliary furnace (see Fig. 1) above the main furnace used to heat the glass sample. The furnaces actually are in close contact to prevent a cool ring section between them, which is accomplished by beveling the edge of the cement toward the center on the auxiliary furnace and outward on the main furnace before firing the cement. This auxiliary furnace is from 4 to 7 in. long (longer for amber glass), it is wound with 0.036-in. diameter tantalum wire imbedded in cement, and it has a center tap so that it may be heated in two sections. The length of the crucible and the number of sections of the auxiliary furnace may be increased if desired. It is convenient to wind a cord between the coils for spacing this small wire. The cord can be removed from the inside when the cement has set. Some thin cement is then placed over and between the wires on the inside; this cement protects the wire and provides a greater radiating area.

After extracting the gases from the glass samples, the main furnace is allowed to cool, and the alkaline deposit in the crucible is heated by the auxiliary furnace. This heating causes the salts (formed when the gases are absorbed by the alkali) to be decomposed and the gases to be set free. When a temperature of about 1100°C. is reached by the auxiliary furnace, the alkali sublimates farther up the crucible. Another fractional decomposition is then made by heating the second section of the crucible in the same way. Table I shows that it is possible to decompose sodium hydroxide, sodium sulfate, sodium carbonate, and sodium sulfite by heating to 1100°C. in a vacuum. The temperature should be raised gradually to between 900° and 1100°C. No attempt was made to obtain a quantitative recovery of gases from these samples but merely to establish the temperature at which the compounds decomposed under these conditions.

The auxiliary furnace is effective in releasing the gases absorbed in alkali volatilized from the glass. It is of little use, however, if alkali is volatilized from the crucible during the outgassing period. The alkali, in such a case, will be deposited above the auxiliary where it cannot be reheated, and a great deal of trouble has occurred from this cause. The sillimanite crucibles recommended by Dalton were used originally; these crucibles occasionally gave out alkali during outgassing, but they were improved when they were refired at cone 32. Crucibles which are made of corundum refired at cone 35 are now being used.

These corundum crucibles are not entirely alkali-free after a long bakeout, but the amount of alkali found is never large and frequently is practically zero. The blank, after outgassing, contains some water vapor and a little sulfur dioxide. Because these gases are in the blank, any alkali in the crucible is assumed to be fairly well conditioned to them.

† Norton Company, cement No. RA563.

TABLE I

DECOMPOSITION OF SODIUM SALTS BY HEATING IN A VACUUM

Substance	Weight (gm.)	Gas expected (cc.)	Gas collected (cc.)	Decomposition started at (°C.)	Little gas obtained above (°C.)
$Na_2SO_4 \cdot 10H_2O$	0.0213	SO_2 1.48 O_2 0.74	SO_2 1.32 O_2 0.594	900	1100
Na_2CO_3	.0038	CO_2 0.804	CO_2 .816	840	1020
Na_2SO_3	.0058	SO_2 1.03	SO_2 .800	900	1100
NaOH	.99	Difficult to weigh and introduce a sufficiently small sample	H_2O too large to measure		950

The apparatus is shown in its present form in Fig. 2. A separate Hyvac and metal diffusion pump, referred to as the shell pump, evacuate the shell surrounding the furnaces. The Pyrex-brand glass tube, called the shell, surrounding the furnaces is sealed at the top by an annular cup of spun copper, which is slipped over the open end and filled with sealing wax. The wax is cooled by passing water through a single loop of $^1/_8$-in. copper tubing placed in the wax next to the glass. This joint must be broken to replace the crucible for each sample run. The wax is softened by an electric heater which fits below the copper dish. The wax must be replaced after it has been reheated about six times or if it accidentally becomes too hot because the constituents of the wax separate and it becomes brittle.

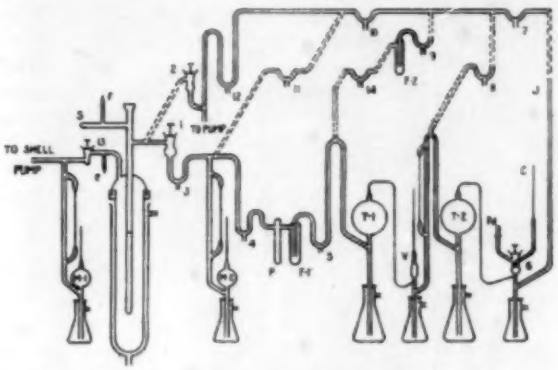

FIG. 2.—Apparatus for gases in glass (broken lines represent horizontal displacement).

The 10-mm. bore, mercury-sealed stopcocks, Nos. 1, 2, and 13, are placed in the lines so that the crucible may be replaced and a new sample may be inserted in sample tube *S* without destroying the vacuum or contaminating any gas sample in the system. Tubes marked *e* and *f* are opened to release the vacuum after closing stopcocks 1, 2, and 13 and are resealed after the new sample and crucible are in place. Tube *e* has now been terminated with a simple stopcock, and this is immersed in a mercury well to prevent leaks.

Stopcock 2 connects a shunt of 15-mm. glass tubing directly from the crucible to the diffusion pump for more rapid outgassing. Most of the analytical line is made of 10-mm. Pyrex-brand glass.

The numbered U-bends are mercury cutoffs for confining gas in any particular part of the system. The open tube on each leads down either to a movable mercury well (described by Prescott[8]) or to a fixed sealed mercury well like those below the McLeod gauges. This well is connected through a 3-way stopcock to the atmosphere to close the valve or to a third vacuum pump to open the valve.

McLeod gauges, *M*-1 and *M*-2, are operated by the third vacuum pump. A Pirani gauge, *P*, in one arm of a Wheatstone bridge, is designed to operate at constant resistance and therefore at constant temperature.[4(b)] The voltage applied to the bridge to balance it is measured with a type-K potentiometer. The freeze-out bulbs, *F*-1 and *F*-2, may be surrounded by cooling agents such as liquid nitrogen or dry ice. Toepler pumps, *T*-1 and *T*-2, are made from 500-cc. flasks, and the wells below them are 1-liter Erlenmeyer flasks. The pumps are arranged to operate automatically by the electric circuit* shown in Fig. 3. The electrical condenser, *C*, must be of such size that it forms a tuned circuit with the particular solenoid valve to which it is connected when the valve is energized. (The writers replaced the valve cores with ordinary tire valve cores.) This can be easily determined by placing a milliammeter of 250-ma. range in the plate circuit and by choosing the condenser that will give a minimum plate current with the valve energized. It must be remembered that the inductance changes as the plunger is drawn into the solenoid. One of the valves used requires a 5-mfd. condenser and the other a 6-mfd. condenser.

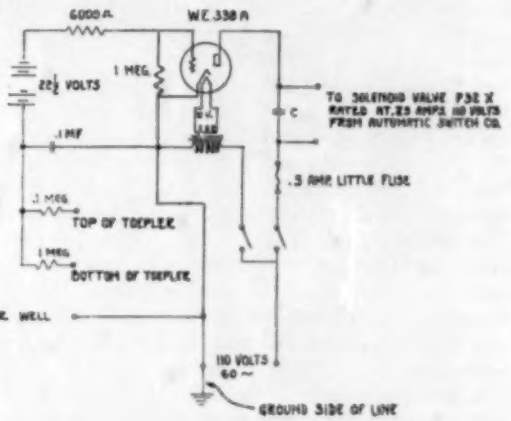

FIG. 3.—Circuit for operating automatic Toepler pump.

Contacts for operating the pump are made by sealing Kovar wire through Pyrex-brand glass No. 706. This glass is joined to Pyrex-brand No. 772, which in turn is joined to the regular Pyrex-brand chemical glass No. 774. If the bottom contact is extended close to the level of the mercury in the well, the Toepler pump will remain open for a longer time. The ground contact in the mercury well is made by sticking an iron wire through the rubber stopper and DeKhotinsky seal to the bottom of the Erlenmeyer flask.

A diffusion pump was not used in the analytical line because the hot mercury vapor might react with sulfur dioxide in the gas mixture.

The single line from the top of the Toepler pump, *T*-1 (Fig. 2), represents the capillary tube through which the gas is discharged from the pump into the volume bulb, *V*. The various gas fractions are measured in this bulb by raising the mercury until the gas

[8] C. H. Prescott Jr., and James Morrison, "Apparatus for Microanalysis of Gas," *Ind. Eng. Chem., Anal. Ed.*, 11 [4] 230–33 (1939).

* This circuit was developed by G. H. Rockwood and applied to a Toepler pump by L. A. Wooten, both of the Bell Telephone Laboratories.

is confined in one of the known volumes and by observing the mercury pressure on the adjacent column. The four known volumes are approximately 0.01, 0.1, 1.0, and 10.0 cc.

Stopcock No. 6 is a special 3-way stopcock with a 4-mm. bore on an angle so that, by raising the mercury through the valve, gas may be confined either in tube *C* or tube *Pd* without trapping any gas in the stopcock. A closed tube of palladium, *Pd*, 2 in. long by $^1/_4$ in. in diameter, is sealed to a platinum cylinder of the same diameter and 1 in. long, which is sealed to soda-lime glass; this glass is then, in turn, sealed by a graded seal to the Pyrex-brand line. The palladium tube is surrounded by a resistance coil and thermocouple so that it may be heated to a definite temperature.[9] With the palladium heated to 270°C., hydrogen will be completely diffused out of the vacuum system into the atmosphere in 20 minutes.

A capillary tube, *C*, is drawn out as needed to remove gas from the vacuum system.† The process is as follows: Mercury is raised below stopcock 6 to cut off tube *J*. From 1 to 25 cu. mm. of gas are pumped from the volume bulb by T-2; the mercury is then raised through stopcock 6, applying compressed air until the height of the mercury in tube *J* is about 70 cm. above the height of mercury in the capillary tube, *C*. Stopcock 6 is now closed, and the mercury is lowered in tube *J*. A slight scratch with a tungsten carbide glass knife below the mercury level enables the capillary to be removed with the gas confined by a slug of mercury. The mercury is lowered in *C* by "cracking" the stopcock, and the open end of the remaining capillary is sealed with a flame or a new capillary is drawn out. Opening to the pump through valves 7, 10, and 12 for five to ten minutes will remove air which entered in sealing.

The line originally contained a tube filled with copper turnings and another tube filled with copper oxide, which has been described by Dalton and others for the analysis of gases not condensable with liquid nitrogen. The hot copper was satisfactory for separating a mixture of oxygen and nitrogen only if the condensable gas (probably CO_2) which comes from the copper was carefully removed. Dalton[4(b)] states that this gas is removed by a liquid air trap. The writers found that the copper and copper oxide tubes were unsatisfactory if the gas mixture contained hydrogen or carbon monoxide. There was always enough oxide on the copper to oxidize these gases, the condensable gas from the copper spoiled the carbon monoxide determination, and water vapor from hydrogen was adsorbed on the walls and could not be measured quantitatively.

III. Procedure in Analysis

A sample of glass to be analyzed is broken into pieces about 3 mm. on an edge and weighed; the usual weight is about 0.7 gm. It is placed in sample tube *S*, a small iron rod encased in glass is placed back of the sample, and the end of tube *S* is resealed with a flame. The iron rod is moved by a magnet at the proper time to push the sample into the crucible, which is sealed in place, and the blowing tube, *f*, is sealed off. Raising mercury in the long U-bend, 12, allows the air to be pumped out through stopcock 2. A Tesla coil is used to test for leaks, after which the furnaces are put in place and the shell is sealed with wax.

After pumping a vacuum in the shell, the main furnace is heated to 1500°C., the auxiliary furnace to 1300° C., and the crucible is outgassed overnight. The following morning, the temperatures are lowered to 1400° and 1100°C., respectively, valve 2 is closed, and a blank is collected for a known time, usually 10 minutes. The blank, which is collected in the same way as a sample, is separated into three fractions, (*a*) gases not condensed with liquid nitrogen, (*b*) gases condensable by liquid nitrogen but not by a supercooled mixture of dry ice and acetone, and (*c*) water vapor. The volume of each fraction is measured. The gases from the blank may be removed for chemical identification or they may be pumped out. As soon as the blank is collected, the power is shut off from the auxiliary furnace so that it may cool before dropping in the sample.

Liquid nitrogen in a Dewar jar is placed around *F*-1; valves 2, 11, 14, and 8 are closed, and the mercury is raised below the volume bulb, *V*, to cut off the outlet to the second Toepler pump. The flint-glass sample is pushed into the crucible a piece at a time, allowing some time for the foam to subside before the next piece is dropped.

For the amber glass sample, the furnace temperature is lowered to 1100° C., the sample is dropped all at once, and the temperature is raised gradually until the viscosity of the glass becomes low enough to allow the gas to escape. The final temperature for amber glass is about 1250°C. The Toepler pump, *T*-1, is allowed to operate until the gas coming over is of the same order of magnitude as the blank. The main furnace is shut off and cooled below red heat. Each section of the auxiliary furnace is then heated to 1100°C. in turn as previously described. The noncondensable gases in the volume bulb are measured, and three portions are removed in separate capillaries for chemical identification.

(1) Chemical Analysis of Noncondensable Gases

The chemical analysis of "noncondensable gases" may be modified, depending on the time available for completion.

For rapid analyses, three capillaries of the noncondensable gas fraction are used. The first capillary is opened under strong potassium hydroxide solution, either by breaking or by forcing the mercury slug out under the solution with a flame. The length of the gas-filled portion is measured, the open end of the capillary is placed in a few drops of the same potassium hydroxide solution in a test tube, and a little pyrogallic acid is added, which absorbs any oxygen present. The second capillary is opened under 1 to 1 hydrochloric acid solution, placed in a test tube in the same way,

[9] E. S. Shepherd, "Analysis of Gases Obtained from Volcanoes and from Rocks," *Jour. Geology*, **33** [3] 289–370 (1925).

† Samples formerly were removed in ampoules sealed off with a flame.

and cuprous chloride is added. This reagent absorbs both oxygen and carbon monoxide. A piece of copper wire is added to prevent the oxidation of the cuprous chloride. The third capillary is opened under colloidal palladium, placed in a test tube containing colloidal palladium, and a few crystals of potassium permanganate are added. This reagent absorbs hydrogen and also takes up oxygen and carbon monoxide when an excess amount of hydrogen is present. Colloidal platinum works about as well as colloidal palladium. These colloidal solutions may be prepared by striking an arc between wires under distilled water.

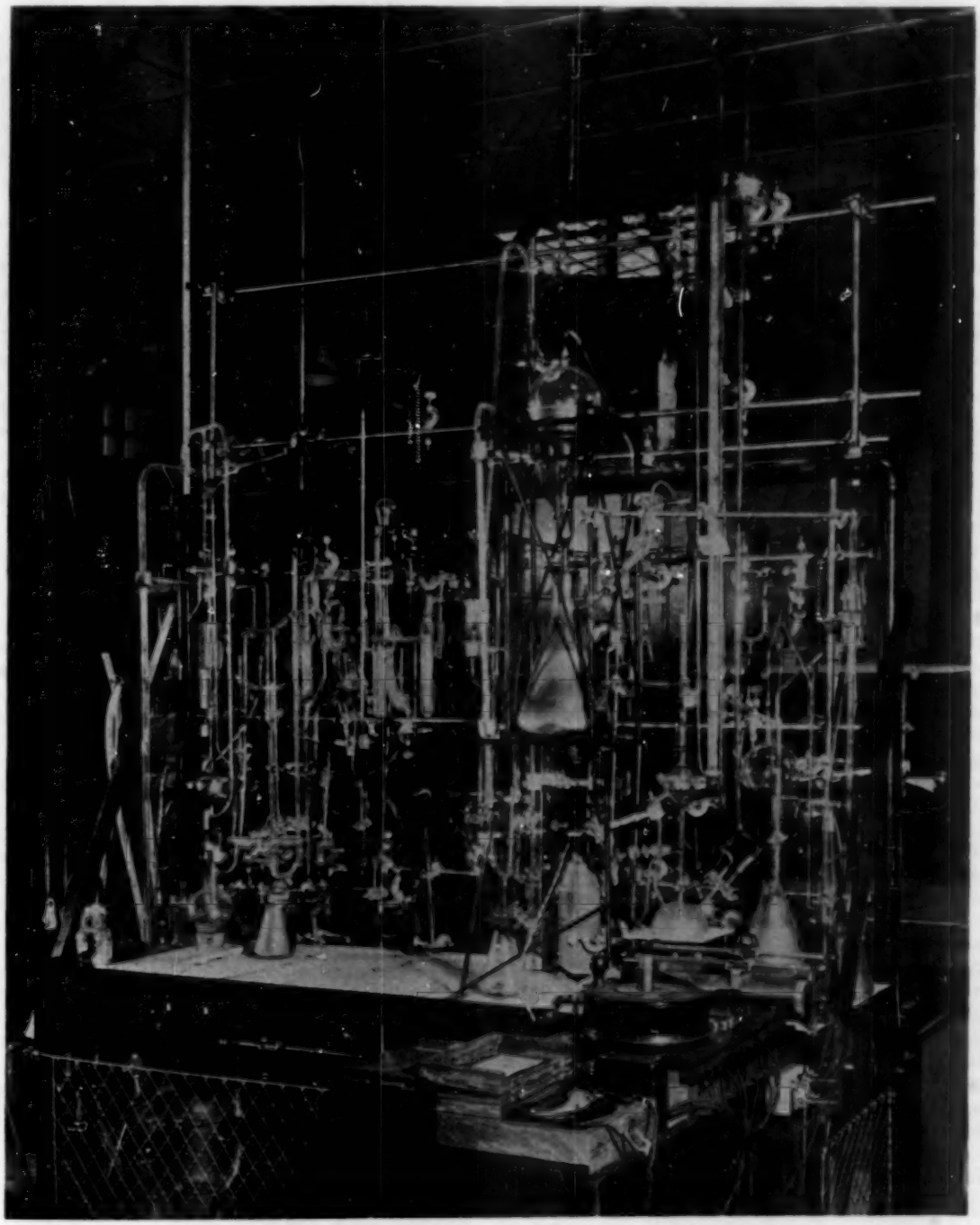

FIG. 4.—Apparatus for gases in glass.

For a second method when more time is available to complete the analysis, a single capillary of the noncondensable gas is used to determine the three gases. Oxygen is first absorbed by placing the capillary in alkaline pyrogallol as described in the procedure for rapid analysis. The following day the capillary is cut, leaving about 1 mm. of liquid to seal the end. It is placed into 1 to 1 hydrochloric acid solution for a few minutes (until the potassium hydroxide is neutralized by the acid through diffusion) and then is transferred to a test tube containing acid cuprous chloride. If any gas remains after a day in contact with the cuprous chloride solution, the capillary is again cut so as to be sealed with 1 mm. of liquid and placed in water for a few minutes to reduce the concentration of hydrochloric acid. This process prevents the acid from dissolving the colloidal palladium. It is then placed into the colloidal palladium, and a few crystals of potassium permanganate are added.

In an alternative method for analyzing the noncondensable fraction when oxygen is known to be absent, the hydrogen is allowed to diffuse out of the mixture through the palladium valve, *Pd*, before the other gases are removed.

(2) Separation of Condensable Gases

The gases retained by the liquid nitrogen trap are confined in the region of the Pirani gage and freeze-out bulb, *F*-1, by closing valves 4 and 5 before removing the liquid nitrogen. A temperature of −135°C. is obtained in the freeze-out bulb by placing an unsilvered Dewar container, partially evacuated and containing a metal sleeve on the inside, around the freeze-out bulb. Liquid nitrogen is placed around this double-walled container. A thermocouple indicates when −135°C. has been attained, and this temperature reduces the vapor pressure of sulfur dioxide to zero. Carbon dioxide is now pumped into the volume bulb and measured. In addition to carbon dioxide, certain other gases come over if they are present; this fraction is therefore referred to as the "CO_2 fraction." Some of the gases which might be included are nitric oxide, nitrous oxide, acetylene, silicon tetrafluoride, boron fluoride, silicon hydride, and hydrogen sulfide. The gases indicated in Table IV have actually been recognized. Chemical analysis has shown, however, that carbon dioxide is the major constituent of this fraction in ordinary flint glass although traces of acetylene have been observed.

Another refrigerant is now placed around the freeze-out bulb to allow sulfur dioxide and any other gases in that fraction to be pumped over, leaving the water vapor. Chemical analysis has shown that sulfur dioxide is the predominant constituent of this fraction. Water has an appreciable vapor pressure at dry ice temperature, −78.5°C. A somewhat lower temperature is conveniently obtained[10] by packing crushed dry ice around the freeze-out bulb, allowing it to stand for a few minutes, and pouring acetone that is precooled to −78°C. over the dry ice. A large negative heat of solution lowers the temperature to about −87°C.; with care, even a lower temperature can be reached. The acetone is cooled by placing it in a metal container on dry ice in a Dewar jar; the acetone, however, must not have CO_2 already dissolved in it. The sulfur dioxide fraction is measured as before, and a sample may be removed for identification.

[10] A. Thiel and E. Schulte, "Binary Equilibrium Systems with Solid CO_2," *Z. Physik. Chem. (Stöchiometrie und Vermandt Schaftslehre)*, **96**, 312–42 (1920).

(3) Water Vapor

Water vapor is determined by placing a constant temperature bath at 35°C. around the freeze-out bulb and the Pirani gage. The bridge is balanced, and the voltage is measured with a type K potentiometer. The amount of water vapor is found from a calibration curve, previously determined, and the water may be identified by its vapor pressure.

To obtain the calibration curve, three bulbs, one containing pure water at 0°C. and the other two of known volume and at room temperature, are connected to the line approximately at the position of the crucible. After evacuating, the calibrated bulbs are filled with water vapor at the vapor pressure of melting ice. The volume of vapor from one or both of the bulbs is transferred to the freeze-out bulb in the usual way. By using two differently sized bulbs and by adding several increments, a calibration curve is obtained. Under these conditions, any adsorption of water vapor on the walls would be the same as in running a sample. The amounts added are calculated on the assumption that the water vapor acts as a perfect gas.

(4) Accuracy with Known Mixtures

The accuracy with which known mixtures may be separated by freezing out constituents has been reported by Dalton for several two- and three-component mixtures. He also showed that air may be analyzed by absorbing the oxygen on hot copper. The writers have checked their procedure by analyzing a four-component mixture; part of this mixture was removed to be used as a standard for testing the accuracy of microanalysis in very small capillaries as described in section VI (3). The remainder of the mixture was analyzed by the freeze-out method, and oxygen was determined in the noncondensable fraction by pyrogallic acid. The original mixture, which had a volume of 0.589 cc., consisted of SO_2 36.7 (by vol.), CO_2 26.5, O_2 24.6, and N_2 12.2%. The volume analyzed was 0.502 cc., and the percentages found were SO_2 35.6, CO_2 27.3, O_2 24.1, and N_2 13.0. The mixture was allowed to remain in the apparatus overnight before analyzing, and there was some evidence of SO_2 having reacted with the mercury. This always happens to a slight extent if a small amount of moisture gets in with the gas.

The writers have successfully analyzed air several times by the copper tube and many times with the pyrogallic acid reagent. The percentage of oxygen obtained with either method was within 0.5% of the correct value.

The palladium tube was installed after it was found that the noncondensable gases from amber glass contain hydrogen and carbon monoxide. To test the

TABLE II
SPREAD OF BLANKS AND OF CHEMICAL ANALYSES OF FRACTIONS*

Sample No.	H_2O†	SO_2† fraction	CO_2† fraction	Noncondensable gases†	SO_2 fraction	Chemical analysis of gas fractions: CO_2 fraction		Noncondensable fraction			
					SO_2	CO_2	C_2H_2	O_2	CO	H_2	R
Flint glass											
146	0.351 ±0.007	0.686 ±0.001	0.017 ±0.004	0.355 ±0.019	0.686	0.017		0.365	0.004		0.005
152	.380 ± .004	.694 ± .002	.014 ± .002	.364 ± .017	.694	.014	0.002	.373			.008
153	.351 ± .003	.735 ± .000	.013 ± .003	.392 ± .016	.735	.014	.001	.402			.006
Amber glass											
137	0.250 ±0.001	0.010 ±0.000	0.005 ±0.000	0.038 ±0.009	0.010	0.002	Present	0.001	0.006	0.040	0.000
139	.245 ± .002	.006 ± .001	.003 ± .001	.038 ± .009	.007	.002	"	.000	.003	.043	.001
141	.268 ± .003	.006 ± .002	.006 ± .002	.037 ± .013	.007	.003	"	.004	.001	.043	.002
142	.270 ± .005	.007 ± .002	.003 ± .002	.038 ± .001	.009	.003	0.001	.001	.002	.032	.004

* All figures are in cc. of gas at standard conditions per gram of glass.
† The ± values represent the extrapolated blank (not deviations from the mean).

TABLE III
AVERAGE DEVIATIONS IN GASES IN GLASS

Sample No.	Glass (gm.)	Crucible	Highest extraction (°C.)	Gases extracted in cc./gm. of glass: H_2O	SO_2	CO_2	C_2H_2	O_2	CO	H_2	R	Total
Flint standard												
146	0.650	Corundum	1400	0.351	0.686	0.017		0.365	0.004		0.005	1.428
152	.771	"	1420	.380	.694	.014		.373			.008	1.469
153	.834	"	1411	.351	.735	.013		.402			.006	1.507
Avg.				.361	.705	.014		.380	.001		.006	1.468
Avg. deviation				± .013	± .019	± .001		± .015	± .001		± .001	±0.027
Amber standard												
137	0.738	Corundum	1340	0.250	0.010	0.002	Present	0.001	0.006	0.040	0.000	0.309
139	.803	"	1250	.245	.006	.002	"	.000	.003	.043	.001	.300
141	.928	"	1150	.268	.006	.003	"	.004	.001	.043	.002	.327
142	.905	"	1256	.270	.007	.003	0.001	.001	.002	.032	.004	.320
Avg.				.258	.007	.003	.000	.002	.003	.040	.002	.314
Avg. deviation				± .011	± .002	± .001		± .002	± .002	± .004	± .001	± .010

palladium tube, a synthetic mixture of these two gases was prepared which contained a larger percentage of carbon monoxide than that reported by Fleiger.[11] Some of the mixture was removed as before to be used in testing by the chemical absorption method.

The volume of the mixture was 0.650 cc., and the mixture consisted of CO 56.3 and H_2 43.7%.

The volume analyzed with the palladium tube at 270°C. was 0.177 cc., and the percentages found were CO 56.0 and H_2 44.0.

A sample of the mixture was also analyzed in a capillary tube by absorbing the CO with acid cuprous chloride. The capillary volume was about 0.010 cc., and the percentages found were CO 56.6 and H_2 43.4.

(5) Method of Deducting the Blank

It has been observed that gases come from the empty crucible only while it is maintained above a red heat or while its temperature is being raised. No gas is given off when the crucible is cold and very little while it is cooling. As stated before, the blank is collected with all parts of the furnace as hot as they will be at any time during the analysis. The amount of gas in each fraction of the blank is calculated to cubic centimeters per minute and multiplied by the total number of minutes that current is going through any part of the furnace. This is called the extrapolated blank. It is a maximum value, inasmuch as all three sections of the furnace are heated in collecting the blank, whereas time is counted for calculating the extrapolated blank when any one section is being heated or is being maintained hot. For this reason, one half of the appropriate blank fraction is arbitrarily subtracted from each gas fraction. This "one-half value" is attached to each corrected figure with a double sign in Table II. The uncertainty due to the blank must lie within these limits; adding the plus or minus value gives the gross amount with no blank deduction, whereas subtracting this value deducts the whole extrapolated blank.

Because the blank gases are collected with the gases from the glass during an analysis, no correction for the blank can be made in the chemical analysis of each gas fraction without running a complete chemical analysis of the blank. This has not been done for the data shown in these tables. The sum of the constituents in the chemical analysis of the noncondensable fraction therefore equals the gross amount of the noncondensable gas, which includes the blank. Table III shows the gross values of each fraction minus one half of the corresponding blank except for the noncondensable gases, where the gross fraction times the percentage of each constituent is given. The values for the carbon dioxide of the amber glass in Table III are found by

[11] A. G. Fleiger, "Use of a Palladium Tube in Gas Analysis," *Ind. Eng. Chem., Anal. Ed.*, **10** [9] 544–47 (1938); *Ceram. Abs.*, **18** [1] 37 (1939).

TABLE IV

GAS CONTENT OF VARIOUS GLASSES*

Sample No.	Glass description	H_2O	SO_2	CO_2	C_2H_2	SiF_4 and BF_3	O_2	CO	H_2	R	Total
98	Flint No. 1	0.485	0.443	0.031			0.164			0.001	1.124
103	Flint No. 2	.269	.412	.033			.171			.000	0.885
104	Special flint No. 3 (with boron and fluorine)	.216	.033			0.504	.000			.011	.764
105	Special flint No. 3 (fluorine content higher than sample No. 104)	.138	.025			1.093	.001	0.004		.011	1.272
110	Flint No. 4 from doghouse	.272	.460	.024			.165			.001	0.922
111	Flint No. 4 from forehearth	.343	.465	.019			.170			.002	.999
112	Flint No. 5 from doghouse	.361	.257	.015			.149			.002	.784
113	Flint No. 5 from forehearth	.368	.268	.013			.166			.001	.816
68	Flint No. 6	.529	.487	.052			.195			.006	1.269
114	Flint No. 6 (developed blisters)	.512	.622	.017			.256			.001	1.408
124	Flint (made in laboratory electric-resistance furnace)	.148	.747	.021			.331			.003	1.250
132	Amber bottle (1357° when sample dropped)	.033	.000	.001			.008	.011	0.217	.003	0.273
142	Amber bottle (1100° when sample dropped)	.270	.007	.003	0.001		.001	.002	0.032	.004	0.320

* All figures in cc. of gas at standard conditions per gm. of glass.

multiplying the gross CO_2 fraction by the percentage of carbon dioxide found by analysis, disregarding the blank in this case.

The data of Table IV are calculated in a similar manner except that only gross values are reported in a few of the earlier analyses. Sillimanite crucibles were used with all samples in Table IV except Nos. 103, 124, 132, and 142 where corundum crucibles were used. The data reported here were obtained from runs in which the alkali from the crucible in general was low. Work is now in progress on the analysis of blanks from corundum crucibles.

IV. Discussion of Results

Table III shows deviations from the mean for gases from flint and amber glasses, respectively. It is evident that the precision of the results is approximately thirty parts per thousand on the total.

Figure 5 shows the relative volumes of gases at normal temperature and pressure extracted from flint glass No. 6 of Table IV. This table gives the gas content of several glasses. It is apparent that the flint glasses contain water vapor, sulfur dioxide, carbon dioxide, oxygen, and a small residue, which confirms the results already reported by Salmang and Becker[3] and by Dalton.[4] The results include any gases left adsorbed on the glass; these, however, are only a small fraction of the total dissolved gases, as shown by Dalton. The sulfur dioxide and oxygen from flint glass appear to come largely from the decomposition of a sulfate.

Samples Nos. 104 and 105 illustrate a case in which the CO_2 fraction contains a large amount of silicon tetrafluoride and boron trifluoride. The gases have similar boiling points and chemical properties so they could not be separated quantitatively with the present procedure.

Samples Nos. 110 through 113 show that there is little change in gas content during fining, which confirms a number of similar comments in the literature. There seems to be some increase, however, in water

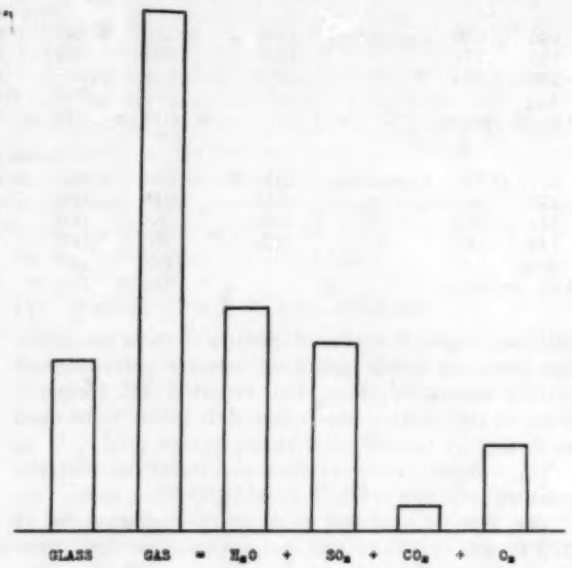

FIG. 5.—Relative volumes of gases dissolved in glass.

content during fining, and this may be caused by the high partial pressure of water vapor in the products of combustion. The relation between water vapor in the glass and in the atmosphere during melting is shown again by comparing samples Nos. 68 and 124. The latter was made from commercial raw materials melted in a resistance furnace in the laboratory instead of under a flame.

The last two samples of Table IV show that hydrogen is obtained from amber bottle glass. Until the temperature of the crucible was lowered to 1100°C. before dropping in an amber sample, no check could be obtained on individual constituents in running duplicates on the same glass. If water vapor was low, the noncondensable gases were high, and only the total gas

content formed any kind of consistent data. Samples Nos. 132 and 142, both cut from the same bottle, illustrate this point.

In running an amber glass at too high a temperature, a mirror oftentimes forms in the glass analytical line above the crucible. By having some previously outgassed water in a sealed tube connected to sample tube *S* through a mercury cutoff, water vapor may be admitted to the crucible, which has been cooled to room temperature, after running the sample. When this is done the mirror disappears, and microscopic examination reveals very small globules of mercury in place of the mirror. Sodium or some other free metal apparently forms an amalgam from the mercury vapor in the system. If now, with liquid nitrogen on $F_2$1 (Fig. 2), valve 3 is opened, a noncondensable gas can be pumped into the volume bulb. This gas has proved to be hydrogen, which shows that the mirror may contain metallic sodium or some free alkali or alkaline earth metal. The mirror has been observed to form several inches above the furnace, and this is in accord with the relatively low boiling point of metallic sodium. When a large mirror is formed, the amber color of the glass is destroyed.

Adding water vapor and, perhaps, other gaseous reagents to the crucible without breaking the vacuum may be a good way to study the various solids that are volatilized from glass when it is heated in a vacuum.

(1) Other Uses of Vacuum Apparatus

One plant, which had a great deal of trouble with blisters in flint glass, finally discovered that the blisters formed when the glass came in contact with a certain kind of refractory. An analysis of the blisters showed them to contain carbon dioxide. A piece of the refractory was placed in sample tube *S*, and, after outgassing, the gases were extracted at 1500°C. There was nothing unusual about the gas content compared to a refractory, which was known to be good. After extracting the gases, oxygen, which was under a pressure about equal to the partial pressure of oxygen in the atmosphere, was sealed in the crucible by closing stopcocks 1 and 2. The refractory was heated to 1500°C. in this oxygen for 2 hours, and the oxygen was pumped out past both freeze-out bulbs surrounded by liquid nitrogen. The carbon dioxide formed by the oxidation of any carbon or carbon compound in the refractory was thus collected with the following results: refractory causing blisters formed 0.126 cc. of CO_2 per gm. and good refractory formed 0.016 cc. of CO_2 per gm.

The small amount of carbon dioxide from the good refractory probably came from the oxygen used. Since the time of that test, Wooten has published a paper[12] in which he states that compressed oxygen contains small amounts of carbon dioxide and hydrocarbons and must be carefully purified. He did this by passing the oxygen through a liquid nitrogen trap, a palladium catalyst at 1000°C., and then through two more liquid nitrogen traps.

[12] L. A. Wooten, "Microgas Analysis Methods and Their Application to Research," *ASTM Bull.*, No. 108, pp. 39–44 (1941).

Part II. Analysis of Gases in Seeds

V. Review of Methods

The attempts to determine gases in seeds lead at once to the consideration of microchemical methods of analysis. A number of papers have appeared on this subject, and various methods of procedure have been devised.[13] Some of these procedures are based on the separation of constituents of a mixture in a vacuum, by fractional condensation or evaporation or by chemical absorption, and others by the selective chemical absorption of the constituents at atmospheric pressure.

Ryde and Huddart[14] have described a procedure for the determination of nitrogen in bubbles in glass by breaking the sample in an evacuated quartz chamber and observing the spectrum excited by a Tesla coil.

Schilling[15] determined the gases present in seeds by grinding the sample under distilled water and by analyzing the gases chemically.

Enss,[16] who developed a method of analysis that permitted the determination of gases in single bubbles, broke the bubble under glycerine and then surrounded it with a series of absorbing reagents.

VI. Procedure of Analysis

The procedure described in this paper is based on an observation made during a visit to the Corning Laboratories. Dalton outlined a method at that time which had been developed in his laboratory for the qualitative determination of sulfur dioxide or of air in seeds. A lathlike section of the sample containing the seed was cut out and drawn into a capillary in a flame; the capillary was then broken under mercury. The gases present in the seed were found to be below atmospheric pressure, and the mercury would therefore be pushed into the open end of the capillary and would serve as a seal. The closed end of the capillary (the end sealed by glass, not mercury) was then touched to a piece of dry ice. If sulfur dioxide was present, it condensed into a liquid and the mercury slug was moved to the bottom of the capillary. If air was present, little contraction was observed.

Dalton at that time was analyzing gases in seeds quantitatively by a different method. It occurred to the writers, however, after a consideration of the

[13] (*a*) N. R. Campbell, "Method for Microanalysis of Gases by Use of the Pirani Gauge," *Proc. Phys. Soc.* [London], **33**, 287–96 (1921).

(*b*) Irving Langmuir, "Chemically Active Modification of Hydrogen," *Jour. Amer. Chem. Soc.*, **34** [10] 1310–25 (1912); see also footnote reference 8.

(*c*) F. E. Blacet and R. A. Leighton, "Microanalysis of Gases," *Ind. Eng. Chem., Anal. Ed.*, **3** [7] 266–69 (1931).

(*d*) F. E. Blacet and D. V. Volman, "Microanalysis of Gases: IV, Nitrous Oxide and Methane," *ibid.*, **9** [1] 44–45 (1937).

[14] J. W. Ryde and R. Huddart, "Analysis of Bubbles in Glass," *Proc. Phys. Soc.* [London], **35**, 197–98 (1923); *Ceram. Abs.*, **2** [8] 176 (1923).

[15] H. Schilling, "Gaseous Inclusions in Glass in Form of Seeds and Bubbles and Their Qualitative Estimation," *Chem.-Ztg.*, **60**, 149 (1936); *Ceram. Abs.*, **15** [8] 233 (1936).

[16] J. Enss, "Analysis of Gases in Glass Bubbles," *Sprechsaal*, **66** [39] 662–66 (1933); *Ceram. Abs.*, **13** [2] 34 (1934).

method just outlined, that it could be developed into a quantitative procedure. The capillary with the gas confined by the mercury slug is obviously similar to the familiar example in physical chemistry of a gas in a closed cylinder with a movable piston. If the gas consists of a single component, a complete condensation would be expected when the closed end of the capillary was lowered to a temperature slightly below the boiling point of the gas confined. If the gas consists of two or more components which are mutually inert, then contractions in volume would be expected which correspond to the boiling points of each of the constituents as the temperature of the closed end of the capillary reaches successively lower temperatures. The amount of contraction in such a case would correspond to the amount of a particular constituent present. The volume of gas exposed to decreasing temperatures should be small compared to the total volume of the sample.

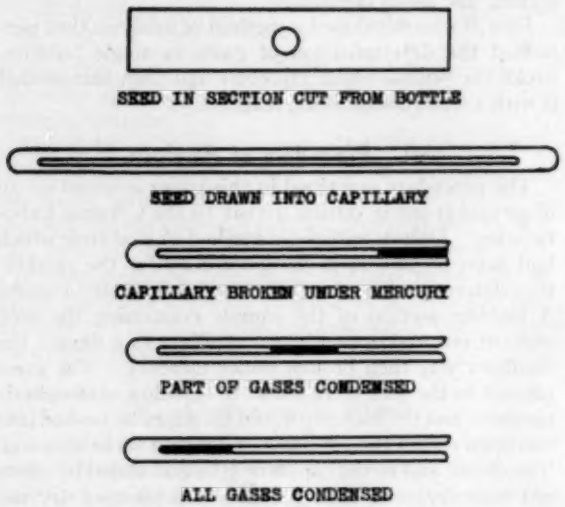
SEED IN SECTION CUT FROM BOTTLE
SEED DRAWN INTO CAPILLARY
CAPILLARY BROKEN UNDER MERCURY
PART OF GASES CONDENSED
ALL GASES CONDENSED

FIG. 6.—Procedure for gases in seeds.

Figure 6 illustrates the procedure which has been outlined. The upper diagram represents a seed in a section of glass cut out of a bottle; this seed may be assumed to contain a two-component mixture of mutually inert gases. The diagrams, in order, then show the seed drawn into a capillary, the result of breaking under mercury, the position of the mercury slug when the closed end of the capillary has been cooled to a temperature slightly below that of the boiling point of one of the constituents present in the mixture, and finally the position of the mercury slug when all of the gases present in the capillary have been condensed.

(1) Apparatus

Figure 7 shows the apparatus used for the analysis of gases in seeds. A metal Dewar flask is fastened to a wooden base, and a strip of copper somewhat longer than the Dewar flask is fastened inside by a copper spring. A copper block is screwed to the end of the copper strip which projects a short distance above the top of the Dewar. The face of this copper block opposite the Dewar has four holes drilled in it, each about 1 mm. in diameter and 2 or 3 mm. deep; a fifth hole is drilled in the end, and a copper constantan thermocouple is cemented into it with DeKhotinsky cement. A rectangular strip of fiberboard, marked with lines 1 mm. apart, is placed on a wooden support, which in turn rests on the wooden base and is fastened flush to the face of the copper block containing the four holes (see Fig. 7).

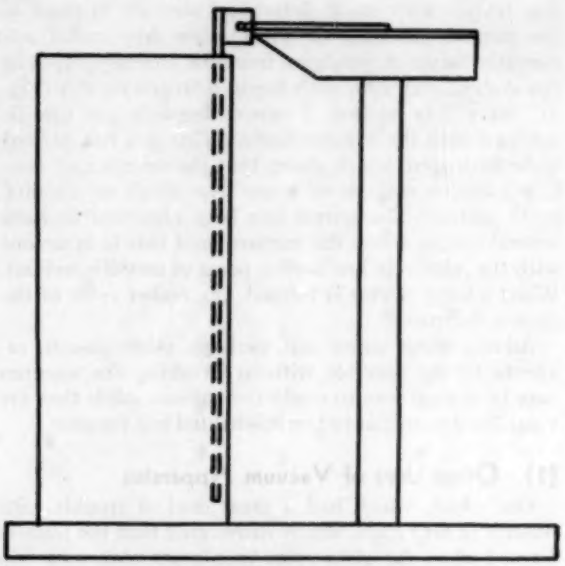

FIG. 7.—Apparatus for gases in seeds.

(2) Procedure

A seed to be analyzed is cut out and studied under the petrographic microscope. Its dimensions may be measured by a Filar micrometer. After the capillary has been drawn and broken under mercury, its length and diameter are measured by the microscope, and the capillary is placed on the fiber strip with about 1 mm. of the end of the capillary in one of the holes in the copper block. The hole is sealed with a little plastic clay. Another capillary containing carbon dioxide is placed on the strip in a similar way to serve as a calibration point for the temperature of the end of the capillary. The temperature of the copper block (and therefore of the end of the capillary) is gradually lowered by pouring small amounts of liquid nitrogen into the Dewar. The decrease in temperature is followed by a semiprecision potentiometer, and the position of the mercury slug by a 10 × hand lens.

The result of an analysis of a mixture of carbon dioxide and nitrogen is shown in Fig. 8. A synthetic mixture of carbon dioxide and nitrogen (respectively 44.2% and 55.8% by volume) was placed in a capillary and broken under mercury. The volume of the sample was about 4 cu. mm. The volume of the mixture showed little contraction as the temperature was lowered until the temperature of about −55°C. was reached (see Fig. 8). A small contraction was then

observed until the temperature of −86°C. was reached, when there wes a sudden contraction to a volume of about 50% of the original; below this temperature, a further and gradual contraction took place. When the temperature was permitted to rise, gradual expansion took place up to about −83°C., then a relatively sharp expansion occurred up to about −80°C., followed by a more or less gradual increase in volume to the original volume as the temperature rose.

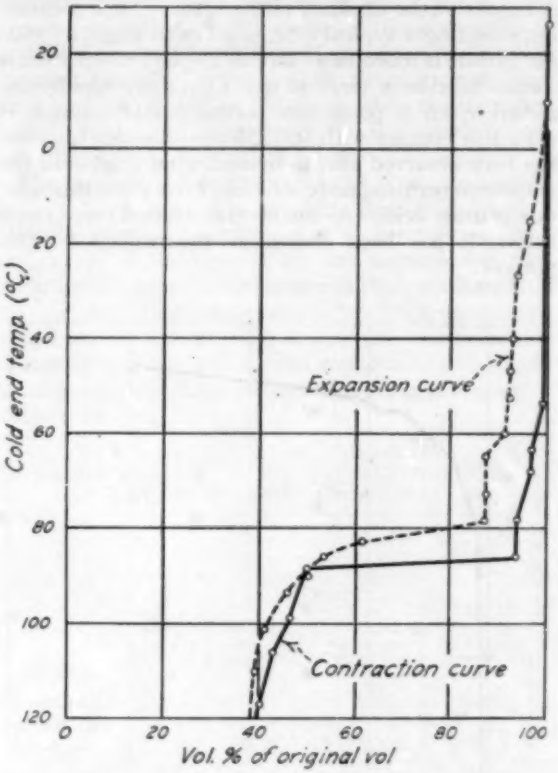

FIG. 8.—Typical curves showing change in volume with temperature of cold end; composition (% by volume), CO_2 = 44.2 and N_2 = 55.8.

The curve shown in Fig. 8 is the result of a single analysis and illustrates a certain lag that is frequently observed in practice. The temperature in this case apparently was lowered a little too rapidly so that contraction took place slightly below the temperature expected, namely, −78.5°C., which is the sublimation point of carbon dioxide. The principal expansion on warming the end of the sample occurred at about −80° C. In an unknown, this action would be taken as a strong indication of the presence of carbon dioxide. The amount of contraction corresponds within a few per cent to the percentage of carbon dioxide in the known mixture if it is measured at the temperature of the principal contraction. This is also true for the expansion curve.

If a sample contains gases which are not mutually inert, the type of contraction curve would then be expected to change from the simple case shown in Fig. 8 to such a curve as (2) in Fig. 9. Curve (1) represents the contraction of a single component, sulfur dioxide, and it shows that complete contraction occurred when the boiling point of sulfur dioxide was reached. Curve (2) represents the result of running the contraction curve on a mixture of sulfur dioxide and air (40% and 60% by volume, respectively). This curve is obviously quite different from that obtained either with the single component or with the 2-component mixture of mutually inert gases. Such a curve indicates that air is soluble in liquid sulfur dioxide, and it confirms the results reported by Dornte and Ferguson.[17] Unless complete data are available on mixtures of this type, it is obviously impossible to attempt a quantitative analysis of the constituents from the curve alone.

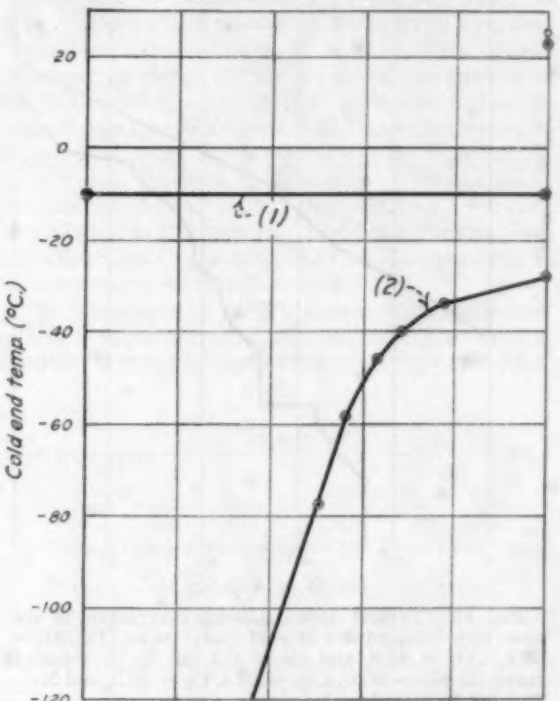

FIG. 9.—Typical curves showing contraction in volume with temperature of cold end; curves (1), SO_2 = 100; curve (2), SO_2 = 40; air = 60 (all % by volume).

This observation is further substantiated by the curves shown in Fig. 10. Curve (1) is a contraction curve of a mixture of sulfur dioxide and carbon dioxide containing a trace of air; curve (2) shows the contraction curve of a 4-component mixture, namely, sulfur dioxide, carbon dioxide, oxygen, and nitrogen. Curve (1) is approximately, but not quite, a straight line; curve (2) shows a number of contractions, more or less irregular, and one sharp contraction of small amount at a temperature (in this case) of −90°C.

[17] R. W. Dornte and C. V. Ferguson, "Solubility of Nitrogen and Oxygen in Liquid Sulfur Dioxide," *Ind. Eng. Chem.*, **31** [1] 112–13 (1939).

These curves illustrate one of the precautions to be taken in attempting to interpret contraction curves of mixtures of several components. Such a contraction might be interpreted as indicating the presence of a small amount of gas having a boiling point at −90°C. According to the tables, silicon tetrafluoride boils at −90°C. It would be obviously erroneous to report the presence of such a gas in this mixture.

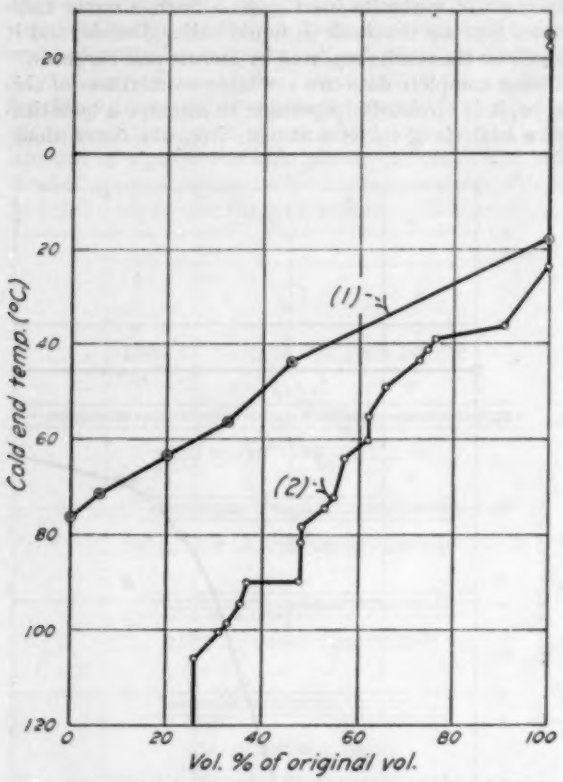

FIG. 10.—Typical curves showing contraction in volume with temperature of cold end; curve (1), SO_2 = 53.8, CO_2 = 45.9, and air = 0.3 (all % by volume); curve (2) SO_2 = 30.6, CO_2 = 20.4, O_2 = 10.3, and N_2 = 38.7 (all % by volume).

This sharp contraction may or may not appear; some curves show it, and others from the same sample do not. It is therefore necessary to confirm the indications obtained from contraction and expansion curves by means of independent tests. Suitable chemical reagents have been selected to determine fairly quantitatively the constituents of mixtures which are evidently mutually reactive. These reagents also serve in some cases to identify the constituent in question. In other cases, additional reagents are used which produce characteristic precipitates that may be identified by the petrographic microscope.

Neutral 1/30 molar potassium permanganate has been found to be a suitable reagent for the confirmation and quantitative determination of sulfur dioxide in a mixture of sulfur dioxide and carbon dioxide or of sulfur dioxide, carbon dioxide, and air. After the contraction curve has been run on the sample, the capillary is removed from the plate and broken under the potassium permanganate solution just ahead of the mercury slug. The potassium permanganate enters the capillary and soon absorbs the sulfur dioxide out of the mixture. The potassium permanganate solution is decolorized, especially at the meniscus in contact with the sulfur dioxide. The rate of reaction may be followed by means of the microscope and a curve may be plotted showing the percentage by volume absorbed by potassium permanganate against time in minutes. A correction for capillary rise is made. Such a curve, respresenting a typical case, is given in Fig. 11. Sulfur dioxide is much more soluble in plain water than is carbon dioxide or air, and it is even more rapidly absorbed when a potassium permanganate solution is placed in contact with it. Carbon dioxide, however, has been observed also to be somewhat soluble in the potassium permanganate solution, even when this solution is made acid. As the neutral solution keeps much better, it has been chosen as the reagent for this purpose.

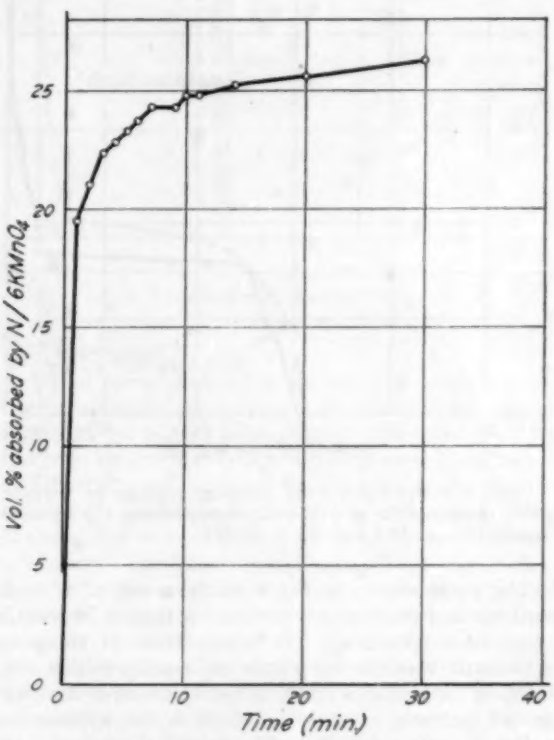

FIG. 11.—Typical curve for absorption of SO_2 by $KMnO_4$ solution; SO_2 = 30.6, CO_2 = 20.4, O_2 = 10.3, and N_2 = 38.7 (all % by volume).

The curve in Fig. 11 shows that a sharp change in slope takes place at a percentage corresponding approximately to the percentage of sulfur dioxide in the known mixture. This change of slope has been taken as the end point of the reaction with sulfur dioxide. The carbon dioxide in the mixture is determined usually by breaking the capillary again, this time under potassium hydroxide solution (about 50%) and observ-

ing the absorption that takes place, which is very rapid. Oxygen, carbon monoxide, and hydrogen are then determined by placing the capillary successively in test tubes containing suitable reagents, as described in section III (1). Samples met in practice, however, are frequently so small in volume that tests for hydrogen at this point are out of the question as well as tests even for carbon monoxide and oxygen.

The identity of the gases present in a sample may be further confirmed by breaking the other half of the capillary under a 10% solution of lead acetate. The presence of sulfur dioxide results in the formation of a white precipitate of low birefringence.[18] Carbon dioxide, however, gives a white precipitate of high birefringence, which is usually readily distinguished with the petrographic microscope. If a sulfide is present, a black precipitate will be formed.

The procedure, briefly, consists of placing a sample, by suitable means, in a capillary tube sealed with a movable piston of mercury and of determining from the nature of the contraction and expansion curves, as outlined, the probable nature of the constituents in the sample. These constituents are then determined quantitatively by chemical absorption, using suitable absorbing reagents, and further confirmed by the study of characteristic precipitates by the petrographic microscope.

[18] E. M. Chamot and C. W. Mason, Handbook of Chemical Microscopy, p. 324, Vol. II. John Wiley & Sons, New York, N. Y., 1931; *Ceram. Abs.*, **10** [8] 608 (1931).

(3) Accuracy

The precision and the accuracy of this method are shown in Table V. It is evident that single components may be determined, with an error of a few tenths of a per cent and with a precision of the same order of magnitude, in samples having volumes of the order of 10 cu.mm. Oxygen in air was determined in samples having volumes of the order of 5 cu. mm., with an error of about 0.4% and a precision of ± 0.8%. Carbon dioxide, in a mixture of carbon dioxide and nitrogen having a volume of the order of about 6 cu. mm., was determined within about 1%. Sulfur dioxide and carbon dioxide in a mixture were determined within about 3% in samples having volumes around 2 cu. mm., and sulfur dioxide and oxygen in a mixture of sulfur dioxide and air were determined similarly with an error of about 2% in volumes of the order of 3 cu. mm.

The error increased as the complexity of the mixture increased, as shown by the results of the analysis of the 4-component mixtures (sulfur dioxide, carbon dioxide, oxygen, and nitrogen). The errors in these cases ranged from about 5% for sulfur dioxide to about 7% for nitrogen, obtained by difference. The volumes of the samples studied ranged from 4.8 to 1.3 cu. mm. The mixture in this case was placed in a glass ampoule and drawn out in the flame into capillaries exactly in the same way as seeds in glass are handled.

The last section of Table V shows results of the analysis of a four-component mixture, having volumes of the order of 2 to 5 cu. mm., when the samples were sub-

TABLE V

ANALYSIS OF SYNTHETIC MIXTURES

Container	Composition by synthesis: Gas	Vol. (%)	Composition by analysis (vol. %): 1	2	3	4	5	Avg. (%)	Precision (%)	Error (%)	Sample vol. (cu. mm.): 1	2	3	4	5
Pyrex-brand capillaries	SO_2	100.0	99.4	99.8	99.9			99.7	±0.2	−0.3					
	CO_2	100.0	100.0	100.0	100.0			100.0	± .0	.0					
	O_2	100.0	100.0	100.0	99.5			99.8	± .2	− .2	16.6	8.1	10.3		
Pyrex-brand capillaries	O_2	21.0	22.2	19.3	19.8	20.6	21.0	20.6	± .8	− .4	5.2	4.8	5.8	5.6	5.3
	N_2	79.0	77.8	80.7	80.2	79.4	79.0	79.4		+ .4					
Soft glass ampoule	CO_2	44.2	44.5	43.6	40.5	44.1	43.1	43.2	±1.1	−1.0	5.8	5.6	5.9	6.3	4.1
	N_2	55.8	55.5	56.4	59.5	55.9	56.9	56.8		+1.0					
Soft glass ampoule	SO_2	27.3	23.3	24.2	24.4			24.0	±0.3	−3.3	1.5	2.2	1.5		
	CO_2	72.5	76.2	75.3	75.1			75.5		+3.0					
	N_2	0.2						0.5							
Soft glass ampoule and capillaries	SO_2	40.0	35.9	42.2	39.6			39.3	±2.2	−0.7	7.3	3.4	2.7		
	O_2†	12.0	15.2	13.7	14.7	12.9		14.1	±0.8	+2.1	2.0	2.1	2.6	2.4	
	N_2	48.0						46.6		−1.4					
Soft glass ampoule	SO_2	30.6	23.6	24.2	27.9	25.2		25.2	±1.4	−5.4	4.8	2.6	1.3	1.4	
	CO_2	20.4	24.4	29.4	23.2	27.6		26.2	±2.3	+5.8					
	O_2	10.3	4.0	3.3	4.2	10.8*		3.8	±0.4	−6.5					
	N_2	38.7	48.0	43.1	44.7	36.4*		45.3		+6.6					
Pyrex-brand capillaries (no flame)	SO_2	36.7	33.2	35.5	31.3			33.3	±1.4	−3.4	2.1	2.9	2.0		
	Total acid gases		57.0	50.3	55.6			54.3	±2.7		2.4	5.2	1.4		
	CO_2	26.5						21.0‡		−5.5					
	O_2†	24.6	27.1	31.3	26.6			28.3	±2.0	+3.7	2.4	5.2	1.4		
	N_2	12.2						18.4		+6.2					

* Omitted from average. † Oxygen determined on separate sample.
‡ Carbon dioxide by difference between average total acid gases and average sulfur dioxide.

jected to no heat whatever. These capillaries were taken individually from tube *C* (Fig. 2) as described and referred to in sections II and III (4). It is evident that the errors are of the same order of magnitude as before, indicating that heating the sample to draw it out into a capillary had little effect on the results obtained. The results for carbon dioxide in this last case were found by determining total acid gases on separate samples and by subtracting the sulfur dioxide from this figure.

It may be said, then, that four-component mixtures of sulfur dioxide, carbon dioxide, oxygen, and nitrogen with volumes of approximately 1 to 5 cu. mm. can be analyzed under room conditions with errors on each component ranging from about 5 to 7%. Table V shows that the precision of the analysis is somewhat better than this. When the volume of the sample, however, is about 1 cu. mm. or less, both precision and accuracy seem to begin to decrease; for example, three samples of the four-component mixture just described were analyzed. One sample had a volume of 1.23 cu. mm., and the other two had volumes of 0.58 and 0.71 cu. mm., respectively. The sample having a volume of 1.23 cu. mm. showed sulfur dioxide to be about 48.9%, which is 18.3% higher than the known value; the other two showed 45 and 32% of sulfur dioxide, respectively. The other components, however, were determined with considerably more accuracy, the average of the three for carbon dioxide being 2% high, the average for oxygen 7.3% low, and for nitrogen 6% low. For volumes below about 1 cu. mm., then, the results should be considered as merely qualitative.

It has proved to be a little difficult to obtain very small samples of known mixtures for the purpose of finding the limits of qualitative tests by this method. Table VI, however, contains data on two commercial samples that were quite small in volume. Sample No. 57 shows that sulfur dioxide can be positively identified in volumes as low as about 0.02 cu. mm., and sample No. 72 indicates that carbon dioxide can be positively identified in samples with volumes as low as 0.005 cu. mm.

The limit of a fairly satisfactory quantitative analysis of the four-component mixtures described is apparently of the order of 1 cu. mm., and the probable limit for the identification of single components at room conditions is of the order of 0.01 cu. mm. When the volumes of samples are much smaller than this, the identifying chemical tests become uncertain. From these experiments, it appears that capillaries having diameters much less than 0.03 mm. and lengths much less than 3 or 4 mm. cannot be handled satisfactorily by this technique.

TABLE VI

ANALYSIS OF GASES IN SEEDS AND BLISTERS

Glass No.	Sample vol. (cu. mm.)	Volume (%) SO_3	CO_2	O_2	N_2 by difference	Precipitate inside seed
	Special commercial flint melt (sample from forehearth)					
54	0.040	100				Absent
55	.014	100				"
56	.036	100				"
57	.019	100				"
58	.009	80				"
	Flint ladle sample					
72	.005	0	100			
	Flint sample from feeder line					
30	.63	0	100			Isotropic present
31		0	100			"
32			97			"
46	.21	0	100			"
47	.02	0	100			Absent
48	.01	0	96			"
	Flint bottle					
8	.38	0	0	2	98	
10	.11	0	0	6	94	
11	.84	0	0	0	100	
13	.44	0	0	20	80	
	Amber bottle No. 1					
20		0	0	0	100	Anisotropic
21		0	0	0	100	Absent
22		0	0	0	100	"
	Amber bottle No. 2					
73	Vacuum					Anisotropic*
74	Almost vacuum	0	0	Trace	Present	Isotropic*
75	0.01	0	0	22†	78	" *

* Precipitate contained sulfite and sulfate.
† O_2 or CO.

FIG. 12.—Deposit inside blister in amber glass.

Table VI shows the results of some analyses of gases in seeds and blisters from commercial samples. The principal component of a special flint sample was found to be sulfur dioxide. In a second set of samples, carbon dioxide was the principal component. These samples were referred to in section IV (1) in connection with the problem of refractories. Other seeds from a flint bottle were evidently due to entrapped air, as oxygen was shown to be present in varying amounts as well as an inert gas, which was reported as nitrogen by difference.

In a number of instances, seeds in amber bottles have been observed which appeared to contain either all nitrogen or practically no gas whatever. A little oxygen occasionally may be found with the nitrogen. These seeds practically always contain a deposit on the inside (see Fig. 12). Other investigators[19] have reported the presence of substances deposited on the inside of seeds. A number of these seeds have been opened, and the deposit has been tested. The deposit was found to contain a sulfate, a sulfite, or both in a majority of cases.

VII. Conclusions

(1) Flint bottle glass contains water vapor, sulfur dioxide, carbon dioxide, and oxygen.

(2) Amber bottle glass contains considerably less total gas than flint glass, and that gas is chiefly water vapor.

(3) Seeds may contain oxygen and nitrogen from entrapped air or in special cases sulfur dioxide or carbon dioxide. In a few instances, other gases have been indicated. The majority of the seeds studied have been found to contain only a single gas.

(4) Seeds, especially in amber glass, have been observed to contain a deposit on the inside, which has been shown to contain a sulfate or a sulfite or both.

Acknowledgments

The authors wish to express their appreciation to U. E. Bowes, Director of Research, Owens-Illinois Glass Company, for suggesting this problem, and to O. G. Burch, in charge of the General Research Laboratory, for helpful suggestions. The problem has been profitably discussed with several members of the staffs of the Geophysical Laboratory, Massachusetts Institute of Technology, the Bureau of Standards, the University of Pennsylvania, the University of Chicago, and the University of Illinois and especially with G. W. Morey, F. G. Keyes, W. A. Weyl, W. D. Harkins, T. F. Young, and A. B. Burg. K. M. Henry, now of the Kimble Glass Company, was actively engaged on the problem at one time and assisted in developing the apparatus and procedures. The authors also acknowledge the assistance received from the Mullite Refractories Company and the A C Spark Plug Company in refiring some of the crucibles used.

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[19] A. J. Holland and Eric Preston, "Microscopic Examination and Identification of Crystalline Products in Commercial Glasses," *Jour. Soc. Glass Tech.*, **21** [87] 395–408 (1937); *Ceram. Abs.*, **17** [9] 304 (1938); see also footnote references 6, 15, and 16.

X-RAY DIFFRACTION AND PHYSICAL PROPERTIES OF POTASSIUM BORATE GLASSES*

By Robert L. Green

Abstract

Data are presented from X-ray studies and from measurements of the physical properties of potassium borate glasses in the composition range from 0 to 40% by weight of K_2O. Calculations based on the X-ray diffraction patterns show a change from three- to four-fold coordination with an increase to 22% in K_2O content. The potassium ions form single-bonded oxygens and thus produce a weakening of the structures with a K_2O content greater than 22%. With 20 to 25% of K_2O, the coefficient of thermal expansion is a minimum, which shows that the majority of the boron atoms are in four-fold coordination. The curves of the composition versus the transformation point, softening point, density, refractive index, and viscosity for 200° to 400°C. also show a change of slope in the composition range of 20 to 30% of K_2O.

The random structure picture as well as the tendency of boron atoms to assume tetrahedral coordination in alkaline borate glasses serve to explain satisfactorily the X-ray diffraction curves and the otherwise anomalous physical behavior of the potassium borate glasses.

I. Introduction

The analysis of X-ray diffraction data is the most conclusive method for determining the atomic structure of glass and its constitution. The method involving a Fourier analysis of the experimental X-ray intensity curve requires no assumptions as to the structure of the glass, and it results in an atomic distribution curve indicating the average number of atoms around any one atom. This treatment has been developed and applied to vitreous SiO_2 and B_2O_3 by Warren, Krutter, and Morningstar.[1] The tetrahedral SiO_4 and the triangular BO_3 configurations have thus been definitely established as the basic units that link together to form the randomly oriented networks that constitute these glasses. In subsequent studies of silicate glasses, only

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(1942)

[1] B. E. Warren, H. Krutter, and O. Morningstar, "Fourier Analysis of X-Ray Patterns of Vitreous SiO_2 and B_2O_3," *Jour. Amer. Ceram. Soc.*, **19** [7] 202–206 (1936).

the SiO_4 tetrahedral arrangement has been found to occur, as in crystalline silicates. Biscoe and Warren,[2] however, have demonstrated that one glassforming oxide is capable of showing a change in coordination, and their report on the structures of the sodium-borate glasses has furnished the basis for this investigation. Their results support the random-structure concept of glass. The distribution curves for these glasses showed that as Na_2O was added to boric oxide some of the boron atoms tended to change from a triangular to a tetrahedral coordination with the surrounding oxygens. This fact (established by a purely mathematical treatment of the X-ray intensity curves) offers some explanation for the anomalies in the physical behavior of borate glasses observed in earlier experiments. Maxima and minima in the physical properties of sodium borate glasses coincide with the compositions in which the greatest number of boron atoms is in tetrahedral configurations. The tetrahedral BO_4 units which join the rest of the network in four directions are able to hold the structure together more firmly than the planar BO_3 structures of boric oxide glass.

X-ray studies have resulted in the clarification of the physical and chemical behavior of simple borate glasses; this line of investigation, therefore, has been continued by determining the atomic structures and the physical properties of a second series of similar glasses. Both sets of measurements have been made on the same glasses to effect better comparison. The properties to be studied are thermal expansion, density, refractive index, and viscosity.

II. Preparation and Analysis of Glasses

Preliminary trials were made to establish the range of glass formation in the K_2O–B_2O_3 system. Fusion of a mixture of K_2CO_3 and H_3BO_3, which contained 40% of K_2O by weight, resulted in a clear glass. When the percentage of K_2O was increased, however, to that of the metaborate (57.4% of K_2O), a fluid melt was obtained, which devitrified immediately on cooling.

Because the range of composition of 0 to 40% of K_2O was considered to be sufficient for this study, glasses containing 10, 20, 30, and 40% of K_2O by weight were made first by the fusion of chemically pure H_3BO_3 and $K_2B_4O_7 \cdot 5H_2O$ in a platinum crucible heated by a Méker burner. When practically all of the bubbles had been removed from the fluid melts, the fusions were stirred thoroughly with a platinum spatula to insure homogeneity. Flat specimens to be used for the measurement of their refractive indices were obtained (after the fusions were uniform) from the glass which adhered to the smooth surfaces of the spatula when it was withdrawn from the melt. Fibers, about 1 mm. in diameter, to be used in the X-ray, thermal expansion, and viscosity studies were drawn after the fusions were cooled to a more viscous state. Slight devitrification tendencies that were observed in the glasses with 20 and 40% of K_2O were avoided by permitting the fusions, which were heated to complete uniformity, to cool undisturbed to the temperature at which the fibers were drawn. Glasses of intermediate compositions, which were needed for the study of a more complete range of physical properties, were prepared by the fusion of weighed, calculated quantities of the four original glasses that were analyzed for K_2O and B_2O_3. These melts were stirred thoroughly and were completely fused as before. No perceptible tendencies for crystallization in the additional glasses with 15 and 25% of K_2O were noticed. To complete the series, boric oxide glass was made by slow dehydration and fusion of boric acid, and specimens were obtained as before. All glasses were numbered according to the approximate percentage of the K_2O present, that is, Nos. 0, 10, 15, 20, 25, 30, and 40. These specimens were cooled and were placed immediately in desiccators over P_2O_5 to prevent atmospheric attack.

For the analysis of the four glasses, Nos. 10, 20, 30, and 40, a method of direct titration was used. The procedure is that given by Rosin[3] for fused sodium borate. The glasses generally were dissolved in water and titrated for K_2O content with standard HCl with methyl orange as indicator. A neutralized solution of glycerine was added, and the B_2O_3 was determined by titration with standard NaOH with phenolphthalein as indicator. The explanation of this method is given by Kolthoff and Sandell.[4] The total $K_2O + B_2O_3$ percentages found by this method were $100 \pm 0.3\%$ in all cases. Inasmuch as the end point of the second titration was not so distinct as the first, the compositions were expressed on the basis of the K_2O which was determined experimentally, and the boric oxide was calculated. These compositions, given in Table I, were used in making up the intermediate glasses, Nos. 15 and 25.

TABLE I

CHEMICAL ANALYSIS OF GLASSES

Glass No.	Per cent by weight		Mol. %	
	K_2O	B_2O_3	K_2O	B_2O_3
10	10.38	89.62	7.9	92.1
20	21.02	78.98	16.3	83.7
30	30.49	69.51	24.4	75.6
40	40.40	59.60	33.4	66.6

III. X-Ray Study and Atomic Structures

Specimens for X-ray diffraction study of the potassium borate glasses were selected from uniform fibers which had diameters calculated to permit maximum diffraction with minimum absorption for the individual compositions. Short lengths of these fibers were centered in vacuum cameras with a radius of about 4.4 cm. The radiation from a Müller tube with a molybdenum target, operated at a peak of 40 kv. and 20 ma., was reflected from a rock-salt crystal at such an angle as to expose the specimens to MoKα. Two diffraction patterns, one with a maximum density of 1.0 and one

[2] J. Biscoe and B. E. Warren, "X-Ray Diffraction Study of Soda-Boric Oxide Glass," *Jour. Amer. Ceram. Soc.*, **21** [8] 287–93 (1938).

[3] J. Rosin, Reagent Chemicals and Standards, p. 385. D. Van Nostrand and Co., New York, 1937.

[4] I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, p. 532. Macmillan Co., New York, 1936. 749 pp.

with a minimum density of 0.30, were obtained for each glass composition. These patterns were microphotometered, and the blackening curves that resulted were changed over to intensity curves by the well-known logarithmic relationship. The X-ray intensity curves, placed on an absolute basis of electron units per unit of composition, are reproduced in Fig. 1 with the curve for vitreous B_2O_3 for comparison. As the K_2O content increases, there is a shift of the first peak to larger angles; with 30% of K_2O, an inner peak begins to show at $\sin \theta/\lambda = 0.08$. In the direction of increasing K_2O, moreover, there is an increase in the heights of the second and third peaks of boric oxide glass although their relative positions remain constant.

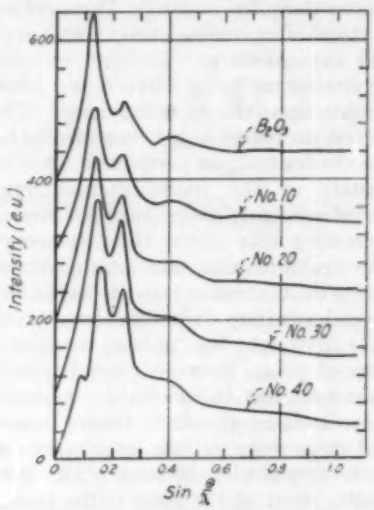

FIG. 1.—Intensity curves for X-ray diffraction of K_2O-B_2O_3 glasses.

Proceeding from these intensity curves, the treatment was essentially that employed in the X-ray diffraction studies of other glasses that have been covered in earlier reports.[5] The $s(i)s$ curves were plotted and integrated, and the radial distribution curves (shown in Fig. 2) were obtained. The areas under the first peaks were determined; the numbers of oxygen atoms surrounding a boron atom were then calculated, and these, with the estimated B–O distances, are given in Table II.

TABLE II

ESTIMATED B–O DISTANCES AND NUMBER OF OXYGEN ATOMS SURROUNDING BORON ATOM

Glass No.	B–O distance (a. u.)	No. of oxygens
B_2O_3	1.39	3.1
10	1.40	3.19
20	1.38	3.65
30	1.42	3.80
40	1.45	3.92

[5] B. E. Warren and J. Biscoe, "Fourier Analysis of X-Ray Patterns of Soda-Silica Glass," *Jour. Amer. Ceram. Soc.*, 21 [7] 259–65 (1938); see also footnotes 1 and 2.

The increase in the B–O distance results from the fact that this value is 1.36 a.u. in triangular coordination, whereas in tetrahedral coordination it is 1.53 a.u.

Inasmuch as there is an increase in B–O distance and in the number of oxygen atoms which surround each boron atom, K_2O appears to effect the production of BO_4 tetrahedra in potassium borate glasses. As K_2O is added to B_2O_3, there is a tendency for some of the triangular BO_3 groups, which compose the structure of boric oxide glass, to change to tetrahedral BO_4 configurations.

The change in B–O coordination, indicated by the radial distribution curves, is continuous with increasing K_2O content. It must be concluded, therefore, on the basis of subsequent studies of the physical properties of these glasses, that only qualitative results are obtained by the X-ray method because of the inaccuracies in the peak areas and positions. The importance, however, of carrying out this X-ray study first is that it indicates, independently, the process of coordination

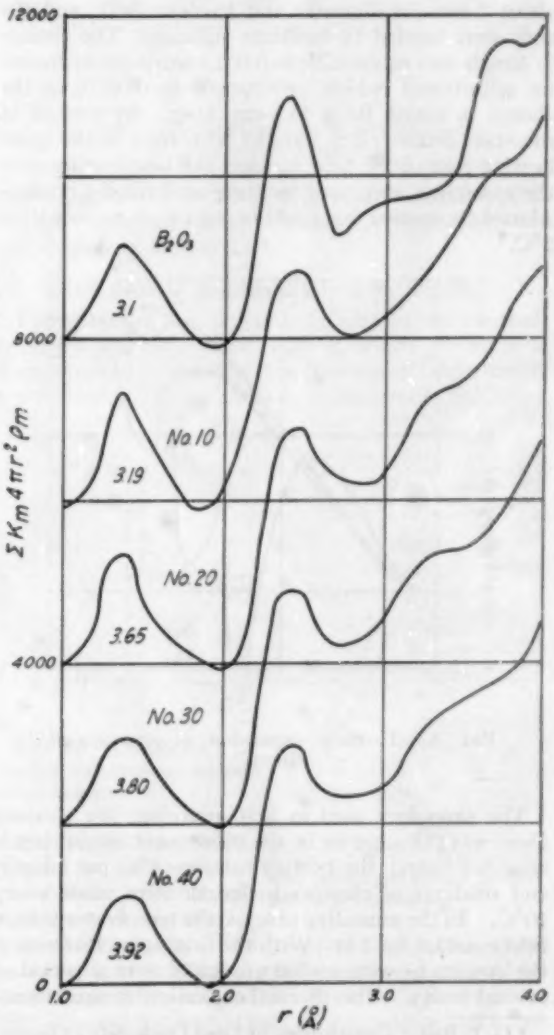

FIG. 2.—Radial distribution curves.

change which the physical behavior can define as to extent and effect.

IV. Physical Properties of K_2O-B_2O_3 Glasses

(1) Thermal-Expansion Method

The thermal expansions of the potassium borate glasses were determined first to obtain the data necessary for annealing the specimens for other tests. The fiber-expansion method, which permits the fiber to expand freely, was used in the hope that further information on the effect of BO_3-BO_4 conversion on the physical behavior could be obtained from the transformation and softening points of these glasses. The fibers were placed in a horizontal tube furnace and heated. Their expansion at various temperatures was determined by means of telescopes focused on the ends of the fibers through glass windows in the furnace walls. The apparatus was the same as that used by Bair[6] in his study of the PbO-SiO_2 glasses, and the diagram and procedure are given with his report. The specimens were fibers about 1 mm. in diameter and 15.3 cm. long, and the ends were beaded to facilitate sighting. The change in length was measurable to 0.002 mm. on the micrometer adjustment, which corresponds to 0.001% of the change in length for a 15.3-cm. fiber. By control of rheostats connected in parallel with each of the three heating coils of the tube furnace, the temperature over the specimens, measured by three calibrated Chromel-Alumel thermocouples, could be kept uniform to within 2°C.

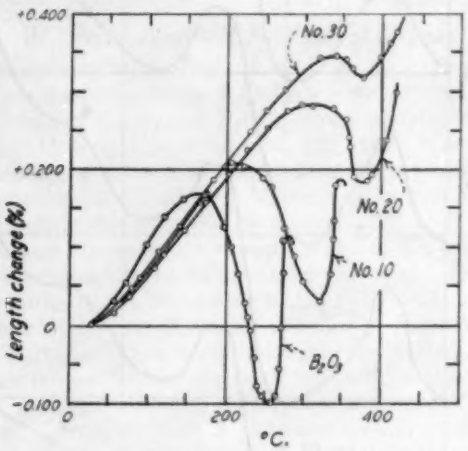

FIG. 3.—Thermal expansion of unannealed fibers.

The procedure used in first annealing the strained fibers was the same as in the subsequent measuring of annealed fibers; the heating rate was 4°C. per minute, and readings of changes in length were made every 20°C. In the annealing process, the temperatures were held constant for 1 hr. With the first signs of softening, the specimens were cooled gradually over a period of several hours. The thermal-expansion measurements were made with the annealed fibers as soon as possible to avoid excessive atmospheric attack. The annealing treatment in each case was satisfactory for the removal of strains because no discontinuities were observed in the curves obtained, particularly in the transformation ranges. The heating rate for the annealed fibers was 4°C. per minute as before.

[6] G. J. Bair, "Constitution of Lead Oxide-Silica Glasses: I–II," *Jour. Amer. Ceram. Soc.*, **19** [12] 339–58 (1936).

(2) Thermal-Expansion Results

Figure 3 shows the expansion curves of the unannealed fibers which were drawn from the fusions of these glasses. The curve for the strained B_2O_3 glass fiber shows definitely the advantage of the fiber-expansion method used; for the first time, the unique behavior of the heated glass is shown during its contraction to a length shorter than the original. These curves, in general, are typical of expansion curves for strained glasses; the initial expansions are followed by contractions while the strains are being relieved and finally by expansions again up to the softening range. The amount of contraction decreases as K_2O is added to B_2O_3. The minima in the contraction portions of these curves fall approximately at the transformation temperatures which are subsequently determined for annealed specimens, indicating that above these temperatures the glasses are unable to maintain internal stresses.

In plotting the thermal-expansion curves for annealed fibers, several arbitrary definitions have been made as follows: (1) A straight line, passing through the greatest number of points between room temperature and the temperature range in which the expansion becomes markedly greater, determines by its slope the coefficient of thermal expansion; (2) the intersection of this line and a second straight line through points leading up to the softening point of the glass is the transformation point; and (3) the temperature at which the fiber first shows signs of sagging is the softening point.

Table III contains the coefficients of expansion and the transformation and softening points for the K_2O-B_2O_3 glasses, which have been determined by these definitions and which have a heating schedule of 4°C. per minute.

The expansion curves are shown in Figs. 4(*A*) and 4(*B*). The first characteristic in the general appearance of the curves is the large amount of expansion between transformation and softening temperatures in glasses with a high B_2O_3 content. This is decreased by the addition of K_2O to a minimum at a composition of about 25% of K_2O. The coefficients of thermal expansion (Fig. 5) are plotted against composition, and a dis-

TABLE III

EXPANSION DATA AND TRANSFORMATION AND SOFTENING POINTS OF K_2O-B_2O_3 GLASSES

Glass No.	α(cm./cm./°C.)	Transformation point (°C).	Softening point (°C.)
B_2O_3	15.93×10^{-6}	247	267
10	13.50 " "	325	350
15	12.14 " "	357	380
20	11.77 " "	408	435
25	11.75 " "	408	437
30	12.49 " "	415	442
40	16.03 " "	423	445

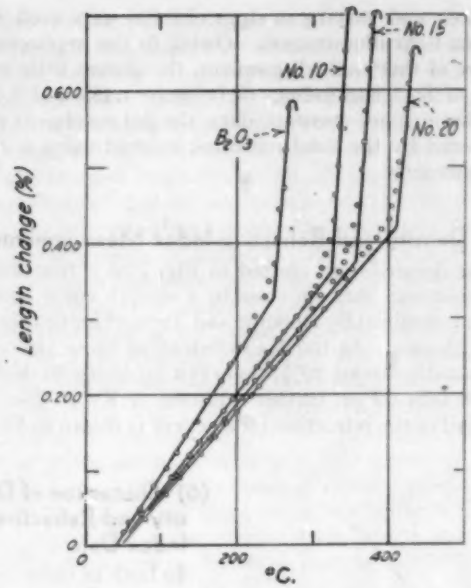

FIG. 4(*A*).—Thermal expansion curves of potassium borate glasses.

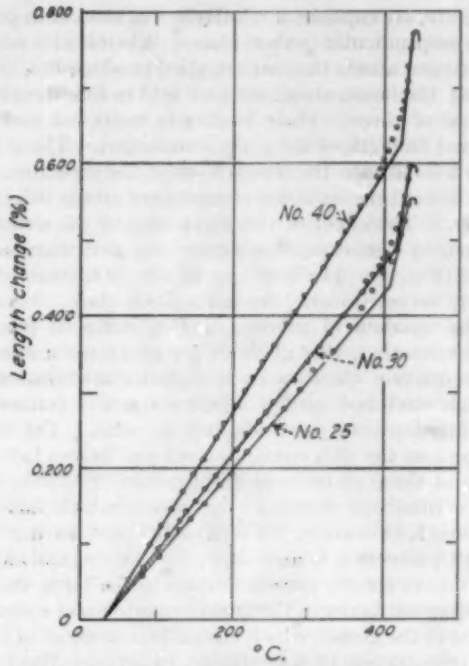

FIG. 4(*B*).—Thermal expansion curves of potassium borate glasses.

tinct minimum is shown at 20 to 25% of K_2O; with 40% of K_2O added, the coefficient again is up to that of B_2O_3 glass. The data for B_2O_3 glass obtained here by the fiber-expansion method agree with the results of Samsoën[7] and Jenckel[8] who used other methods. The potassium borate glasses, in general, show higher coefficients of expansion than the corresponding soda-borate glasses on the basis of the data by Gooding and Turner.[9] To check these data, a glass with 30% of Na_2O was prepared by fusing borax in a platinum crucible; fibers were drawn and the coefficient of expansion was determined by the same experimental procedures as before. This value was found to be 12.36×10^{-6} cm. per cm. per °C., which agrees with the value of 12.22×10^{-6} which Gooding and Turner found in the range 120° to 240°C. The corresponding molar composition in the K_2O-B_2O_3 series (No. 40) has an expansion coefficient of 16.03×10^{-6}. This behavior is the reverse of that found when these alkalis are used in silicate glasses.

The transformation and softening temperatures are shown in Fig. 6 to be functions of the K_2O content. The temperature interval between the two curves is seen here to be approximately constant. There is a rapid rise in both curves as K_2O is added up to about 20%; with amounts of K_2O above 20% there is little change. Jenckel[8] found that the Na_2O-B_2O_3 and BaO-B_2O_3 glasses behave similarly. According to his results, the rise from 20 to 40% of K_2O would be followed by a drop in these curves for glasses that contain more than 40% of K_2O.

(3) Discussion of Thermal-Expansion Results

The results of the X-ray study explain the thermal-expansion curves; when K_2O is added to B_2O_3, a change from 3 to 4 in the coordination of boron atoms is produced. The problem is to determine the effect which this change will have on the glasses that are subjected to the disrupting forces produced by thermal agitation. In the structure of B_2O_3 glass, the network of linked BO_3 units is loose and collapsible. Each boron atom, bonded to the network through the three adjacent oxygens, is held only in a plane and is not restricted in a third dimension. The BO_3 configurations,

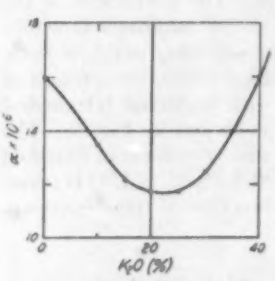

FIG. 5.—Coefficient of thermal expansion (composition curve).

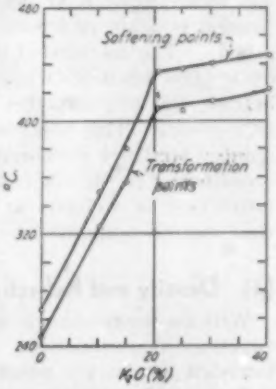

FIG. 6.—Transformation and softening points (composition curves).

[7] M. O. Samsoën, "Anomaly in the Expansion of Glass B_2O_3," *Compt. rend.*, **181**, 354 (1925).

[8] E. Jenckel, "Temperature of the Transformation Intervals of Glasses Formed from B_2O_3 with Na_2O and BaO," *Z. Elektrochem.*, **40** [7b] 541 (1934); *Ceram. Abs.*, **14** [6] 137 (1935).

[9] E. J. Gooding and W. E. S. Turner, "Study of the Series of Glasses Containing Sodium Oxide, Boric Oxide, and Silica," *Jour. Soc. Glass Tech.*, **18** [69] 32–66 (1934); *Ceram. Abs.*, **13** [9] 234 (1934).

therefore, are capable of relatively free motion in directions perpendicular to their planes. When K_2O is added, the oxygen atoms that are supplied produce BO_4 tetrahedra; the boron atoms are now held in four directions instead of three. Their motion is restricted and the internal strength of the glass is increased. The potassium ions fit into the many holes of the structure and tend to hold the adjacent groupings of atoms still more firmly. The effect of this tightening of the structure is seen in the expansion curves for the unannealed fibers (Fig. 3). The looseness of the BO_3 structure is clearly revealed in the curve for B_2O_3 glass. Because of the freedom of motion of BO_3 units in relation to one another, this glass shows an extreme amount of contraction when the cooling strains are released, as though stretched springs which connect a framework of hinged planes were allowed to relax. The extra oxygens in the BO_4 configurations put braces between some of these planes and the looseness is partly lost; this contraction decreases for glasses which have increasing K_2O content. The mobility and looseness of the BO_3 structure is also shown by the thermal-expansion curves for the annealed fibers in the large amount of expansion between the transformation and softening points of the glasses which have a high content of B_2O_3. The introduction of K_2O appears to decrease this looseness proportionately as BO_4 groupings form. The same reasoning applies to the thermal-expansion coefficients of annealed fibers as plotted in Fig. 5. The coefficients decrease on adding K_2O up to about 22% because the BO_4 tetrahedra are being formed in this range, and they brace the structure and diminish the extensibility of the former planar BO_3 network. With this strengthening, the structure is less capable of stretching under thermal agitation forces. In the range of 20 to 25% of K_2O, however, the formation of BO_4 tetrahedra decreases; an increased amount of K_2O weakens the structure, breaks the B–O–B bonds, and forms weak K–O bonds. The coefficient of expansion is again increased, and a minimum is established. The increase in the softening point of boric oxide glass when K_2O is added shows the process of bracing the BO_3 structure with scattered tetrahedral BO_4 groups. This process is shown in Fig. 6. The reduced tendency for boron atoms to form in four-fold coordination in the range of 20 to 25% of K_2O is manifested here by a change in direction of these curves in this range of composition.

(4) Density and Refractive-Index Methods

With the information now available from the thermal-expansion determinations, several pieces of each glass intended for density measurement and the flat specimens for index measurement were annealed. This was done by holding each composition for 1 hr. at a temperature midway between its transformation and softening points and then cooling gradually. The densities were determined for material between 20- and 100-mesh in size by the pycnometer method, using kerosene, and measurements were made at 25°C. In first measuring the refractive indices of the potassium borate glasses, immersion liquids prepared from kerosene fractions and varying in steps of 0.005 were used with sodium light illumination. Owing to the approximate nature of this method, however, the glasses with 10 to 25% of K_2O had indices of between 1.485 and 1.490. To obtain more accurate data, the flat specimens were measured by the total reflection method using a Zeiss refractometer.

(5) Density and Refractive-Index Measurements

The densities are plotted in Fig. 7 as a function of composition; they lie close to a smooth curve similar to that obtained by Gooding and Turner[9] for the Na_2O-B_2O_3 glasses. As the K_2O content of these glasses is increased to about 20%, there is a rapid rise in density which falls off on further addition of K_2O. The rise and fall of the refractive-index curve is shown in Fig. 8.

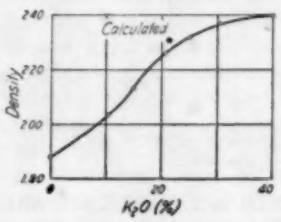

FIG. 7.—Density of potassium borate glasses

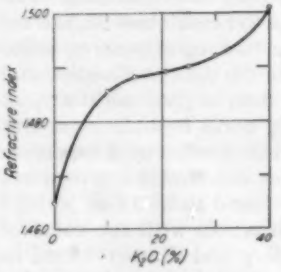

FIG. 8.—Index of refraction of potassium borate glasses.

(6) Discussion of Density and Refractive-Index Data

In both of these properties, the rise in the curve from the B_2O_3 side is due to the formation of BO_4 tetrahedra which join the structure together more firmly and hold the boron atoms involved to the rest of the network in three dimensions. It is this tying together of the structure that decreases the volume of the glass and thus tends to produce a greater increase in density and index than could be due solely to the greater molecular weight of K_2O. Beyond the composition that contains 22% of K_2O where the maximum change to BO_4 groups has occurred, the curves level off as the tendency for boron atoms to assume four-fold coordination declines. The method developed by Warren and Biscoe[2] was used to determine the density of the composition $K_2O \cdot 5B_2O_3$, wherein the boron atoms in the theoretical component $K_2O \cdot B_2O_3$ are assumed to be in four-fold coordination and the remainder in triangular; the density of this glass was calculated to be 2.305 gm. per cc. The experimental value here for this glass with 22.5% of K_2O is 2.275 gm. per cc., indicating the proper magnitude of density change.

(7) Viscosities of K_2O-B_2O_3 Glasses

Determinations of the viscosities were made over a temperature range immediately below the transformation intervals of the glasses. The fiber method was employed with a procedure similar to that used by

Lillie.[10] Glass fibers, approximately 1 mm. in diameter and 250 mm. long, were carefully calipered and suspended vertically in a furnace. This furnace, which has been described by Norton,[11] permits the maintenance of constant temperatures over the lengths of the specimens for periods of days.

The internal strains produced in drawing the fibers were removed first by an annealing treatment, and the temperature was then lowered to that at which measurements were to be made. Loads were applied after the specimen had been kept at the desired temperature for periods of time ranging from several days at lower temperatures to several hours near the transformation ranges. Following the rapid rate of extension on the first application of the loads, the elongation reached a constant rate, which was determined by readings at regular intervals, that is, every several minutes for the higher temperatures and at intervals of several hours for the lower. Owing to the large amount of extension which B_2O_3 glass and those compositions high in B_2O_3 showed, correction for the changes of length was made, and the diameters of the fibers were again determined after the runs.

(8) Results of Viscosity Data

For calculating the viscosities of the glasses at the varying temperatures, Lillie's equation was used.

$$\eta = \frac{60l\,mg}{3\pi r^2 S}$$

η = viscosity (poises).
l = length of fiber (cm.).
m = total suspended weight (gm.).
g = gravitational constant.
r = radius of fiber (cm.).
S = constant rate of elongation (cm./min.).

The logarithms of the viscosities are plotted for each composition as functions of temperature to obtain the linear relationship of viscous flow (Fig. 9). The essential feature here is the variation of viscosities with composition changes. For the same viscosity, a much greater rise in temperature is needed between boric oxide glass and the K_2O-B_2O_3 glass with 20% of K_2O than is required between the latter and the glass with 40% of K_2O; for example, the logarithms of the viscosities are plotted against composition for definite temperatures (see Fig. 10). This method represents only the trends, inasmuch as it has required the assumption that the linearity in the log viscosity-temperature curves extends beyond the range actually covered by experiment. This family of curves resembles those of Fig. 6 and shows a rapid rise in isothermal viscosities from B_2O_3 up to about 22% of K_2O and is followed by a leveling off of the curves.

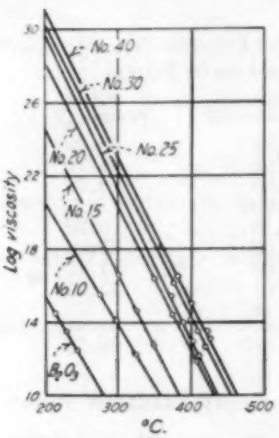

FIG. 9.—Viscosity of potassium borate glasses.

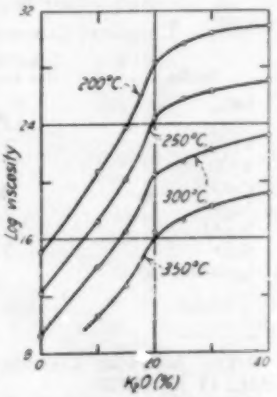

FIG. 10.—Log viscosity (composition curves).

(9) Discussion of Viscosity Results

The effect of K_2O in producing a firmer, more rigid structure when it is introduced into boric oxide glass is clearly shown. Owing to the formation of BO_4 tetrahedra, the structures tend to resist deforming stresses at any given temperature in proportion as these interlocking groups are produced. The coefficients of thermal expansion have shown that the tendency toward BO_4 formation falls off at 22.5% of K_2O, and the change in direction of the curves of Fig. 10 may be thus attributed to the weakening of the structure caused by the production of single-bonded oxygen atoms in glasses with a K_2O content greater than 22.5%.

V. Conclusions

(1) X-ray studies of the structures of K_2O-B_2O_3 glasses show that the boron atoms change coordination from 3 to 4 as the K_2O content is increased.

(2) This change from BO_3 to BO_4 falls off as the K_2O content exceeds about 22%, as shown by the curve for the coefficient of thermal expansion, which is at a minimum for this composition.

(3) The formation of BO_4 tetrahedra strengthens the loose BO_3 structure of boric oxide glass in the K_2O-B_2O_3 glasses and is accompanied by a rapid rise in their transformation and softening points and isothermal viscosities as the K_2O content is increased up to about 22%.

(4) The potassium ions form single-bonded oxygens and thus produce a weakening of the structures with a K_2O content greater than 22%.

(5) The density and refractive-index curves have greater increases in the range of composition from 0 to 22% of K_2O, owing to the formation of BO_4 tetrahedra and the consequent tightening of the glassy network.

Acknowledgment

The author wishes to acknowledge the assistance of F. H. Norton for his supervision of the work on the physical properties of these glasses; of B. E. Warren, who directed the X-ray studies; and of Jonathan Biscoe in the experimental and theoretical development of the X-ray method.

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[10] H. R. Lillie, "Viscosity of Glass Between the Strain Point and Melting Temperature," *Jour. Amer. Ceram. Soc.*, **14** [7] 502–11 (1931).

[11] F. H. Norton, "Measuring the Viscosity of Glass," *Glass Ind.*, **16** [5] 143–44 (1935); *Ceram. Abs.*, **14** [7] 160 (1935).

NEPHELINE SYENITE IN HOTEL CHINAWARE BODIES*

By C. J. Koenig

Abstract

A series of hotel chinaware bodies, based on a commercial body composition, was prepared. The greater fluxing activity of nepheline syenite compared to potash feldspar was compensated for (1) by lowering the firing temperature, (2) by reducing the amount of the principal flux, and (3) by reducing or eliminating the auxiliary flux.

I. Introduction

The purpose of this study was to obtain data which would serve as a guide for the use of nepheline syenite in hotel chinaware bodies. The physical properties of nepheline syenite and the application of this material in other types of ceramic products have been discussed previously.[1] The greater fluxing activity of nepheline syenite compared to potash feldspar was compensated for in this study (1) by lowering the firing temperature, (2) by reducing the amount of the principal flux, and (3) by reducing or eliminating the auxiliary flux. In china bodies that are formulated with English clays, the procedure for compensating for the fluxing activity of nepheline syenite would be to replace such clays with the more refractory American clays. Substitutions of this type, however, are not included here because only American clays were used in the commercial hotel china body composition on which these studies were based.

II. Experimental

The bodies were prepared in batches of 50 lb., dry weight. The ball clays were crushed to $^1/_2$-in. size and were soaked overnight before blunging. The dolomite was preground with 10% of clay for 3 hr. in laboratory ball mills. The body slips were filter-pressed, wedged to the desired consistency, and formed into the several types of specimens.

Aliquot portions of the various test specimens were fired as follows: (*a*) cone 7, glost kiln, (*b*) cones 9 to 10, semivitreous bisque, and (*c*) cone 11, hotel china bisque.

The comparative chemical compositions of the Lakefield nepheline syenite and of the potash feldspar are given in Table I.

The hotel china bodies which were prepared are described as follows: Body No. 1†, comparative feldspar body; body No. 2, direct substitution of nepheline syenite for feldspar; body No. 3, feldspar replaced with nepheline syenite and 2% of flint; body No. 4, feldspar replaced with nepheline syenite, 3% of flint, and 1% of ball clay; body No. 5, nepheline syenite replaced feldspar and dolomite content (1% more of clay than bodies Nos. 1 to 4 at expense of flint); and body No. 6, nepheline syenite replaced feldspar and two thirds of the auxiliary flux content was replaced by flint (same clay content as body No. 5).

Standard methods, apparatus, and calculations were used in making these tests.[2] The thermal-expansion determinations were made on fired bars with a fused-quartz expansion apparatus designed by the National Bureau of Standards.[3] The sag tests were made by firing horozontally solid cast specimens, $^1/_2$ by 2 by 8 in. in size, on supports set 6 in. apart. The sag index of the body under fire is represented by the ratio of deflection to the span (6 in.) multiplied by 100. The pitch was determined with a wave meter used in conjunction with a cathode ray oscillograph and an audio oscillator.[4] The frequency was measured directly in cycles per second, and the glaze-compression data were obtained by the ring test method originated by Schurecht and Pole.[5]

III. Results and Discussion

The physical properties of the bodies are given in Table II. The dry strength of the bodies fell approximately in the same range, that is, from 164 to 187 lb. per sq. in.

Table I

Chemical Compositions of Fluxes

Oxides	Lakefield nepheline syenite (%)	Potash feldspar (%)
SiO_2	60.24	65.90
Al_2O_3	24.05	18.70
Fe_2O_3	0.06	0.08
TiO_2	0.002	
CaO	0.15	0.20
MgO	0.02	Trace
Na_2O	10.03	1.70
K_2O	5.01	13.00
Ignition loss	0.46	
Total	100.022	99.58

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 3, 1941 (White Wares Division). Received April 3, 1941.

[1] (*a*) C. J. Koenig, "Nepheline Syenite in Ceramic Ware," *Ohio State Univ. Engr. Expt. Sta. Bull.*, No. 103, 74 pp., 1939.
(*b*) C. M. Nicholson, "Developing Canada's Nepheline Syenite," *Can. Mining Jour.*, **61** [3] 135–46 (1940).
(*c*) H. J. Orlowski and C. J. Koenig, "Thermal Expansion of Silicate Fluxes in the Crystalline and Glassy States," *Jour. Amer. Ceram. Soc.*, **24** [3] 80–84 (1941).

† Composition not given at request of manufacturer.

[2] The American Ceramic Society Standards Report, *ibid.*, **11** [6] (1928).

[3] Peter Hidnert and W. T. Sweeney, "Thermal Expansion of Magnesium and Some of Its Alloys," *Bur. Stand. Jour. Research*, **1** [5] 771–92 (1928); R.P. 29; *Ceram. Abs.*, **8** [1] 65 (1929).

[4] S. V. Forgue and G. A. Loomis, "Modulus of Elasticity of Dinnerware Bodies by the Sonic-Vibration Method," *Bull. Amer. Ceram. Soc.*, **20** [12] 425–30 (1941).

[5] H. G. Schurecht and G. R. Pole, "Methods of Measuring Strains Between the Glazes and Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **13** [6] 369–75 (1930).

The direct substitution of nepheline syenite for potash feldspar used in body No. 2 resulted in an absorption of 0.6% at cone 7 compared to 2.9% in feldspar body No. 1 (see Fig. 1). Body No. 2 was vitreous at cones 9 to 10 (it was probably vitreous at a lower temperature). Body No. 2 had the highest strength of all of the bodies when it was fired to cones 9 to 10 (see Fig. 2); at this temperature, however, it showed more warpage than the other bodies. Figures 3 and 4 show that there was not much difference in the thermal-expansion data on these bodies. This agreement is also true of the glaze-compression data (see Table II).

Body No. 4 (with 4% less nepheline syenite) showed about the same absorption as body No. 1 (feldspar) at the lower temperature. It was not quite so vitreous as body No. 1 at cone 11, however, which is indicated

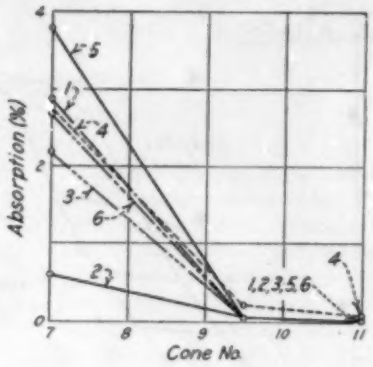

FIG. 1.—Absorption.

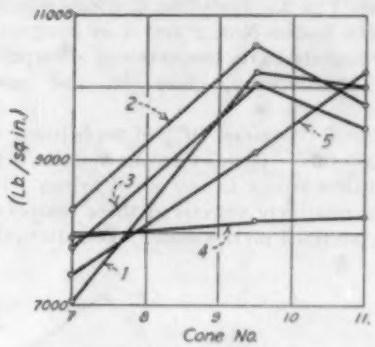

FIG. 2.—Modulus of rupture.

TABLE II

PHYSICAL PROPERTIES (DRY AND PLASTIC)

Property	Cone No.	Body No. 1	2	3	4	5	6
Water of plasticity dry basis (%)		26.1	25.9	26.1	26.5	24.0	25.5
Linear drying shrinkage dry basis (%)		4.8	5.0	4.8	5.2	4.4	5.0
Volume drying shrinkage dry basis (%)		14.0	15.1	15.1	16.3		16.4
Dry strength (lb./sq. in.)		164	176	164	187	176	160
Linear firing shrinkage dry basis (%)	7	8.1	8.8	8.3	8.0	6.7	7.4
	9–10	9.18	9.02	9.1	9.1	8.7	9.1
	11	9.09	8.9	8.9	9.05	8.7	9.0
Volume firing shrinkage dry basis (%)	7	26.6	27.6	27.4	26.4	22.0	24.1
	9–10	28.7	27.9	28.2	28.1	27.2	28.6
	11	28.2	27.2	27.3	27.5	27.2	28.4
Absorption (%)	7	2.9	0.6	2.2	2.7	3.8	2.8
	9–10	0.04	0	0.06	0.2	0.02	0
	11	0.0	0	0	0.06	0	0
Modulus of rupture (lb./sq. in.)	7	7020	8320	7800	7900	7400	6800
	9–10	10200	10600	10000	8100	9100	9000
	11	10000	9700	9400	8200	10100	10250
Modulus of elasticity (million lb./sq. in.)	9–10	10.0	9.7	9.1	8.6	9.2	
	11	9.3	9.7	9.6	8.0	9.0	
Sag index	9–10	4.5	4.7	3.7	3.0	2.4	
	11	3.3	3.7	4.3	3.3	2.3	
Pitch frequency (cycles)	7	1007	1091	1055	1057	985	
	9–10	1199	1263	1197	1130	1160	
	11	1215	1254	1245	1158	1209	
Translucency (in.)	7	0.21	0.26	0.24			
	9–10	0.35	0.40	0.35	0.31	0.29	0.31
	11	0.34	0.38	0.36	0.34	0.30	0.32
Glaze fit compression (mm.) commercial glaze, cone 6)	11	0.060	0.064	0.076	0.092	0.080	

Property	Cone No.	Body No.					
Order of ink stain resistance (from best to poorest)	9–10	2	3-1	5	6	4	
	11	2	3	6-1-5	4		

by the bisque absorption. Strangely enough, body No. 4 was the only one to show blistering when it was glazed and glost fired, which must have been the result of a different glaze-body interaction inasmuch as the bisque was definitely not overfired.

Body No. 4 warped less than any of the bodies that contained the normal auxiliary flux content. The strength of this body fired at the higher temperatures was only fair. The glaze-compression data indicate that body No. 4 had a higher thermal expansion than bodies Nos. 1 or 2. Body No. 3, which was intermediate between bodies Nos. 2 and 4 in composition, was also intermediate in its properties of absorption, pitch, warpage, translucency, glaze fit, and modulus of elasticity.

Body No. 5 contained 19% of nepheline syenite and no auxiliary flux. It was vitreous at cones 9 to 10 and showed little warpage in any of the firings. The glassy phase was relatively viscous at these temperatures because it contained no dolomite. The strength of body No. 5 at cone 11 was equal or better than that of body No. 1, and its thermal expansion was a little higher than that of body No. 1 (Fig. 5). The regular glaze on body No. 5 was under more compression than that on body No. 2; high compression glazes, however, are known to be desirable. The modulus of elasticity of body No. 5 was lower (more elastic) than body No. 1 at cones 9 to 10 and slightly lower at cone 11, and it was not quite so translucent as body No. 1.

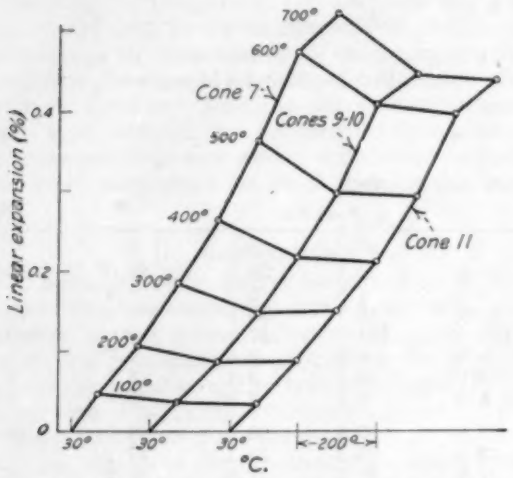

FIG. 3.—Thermal expansion of body No. 1.

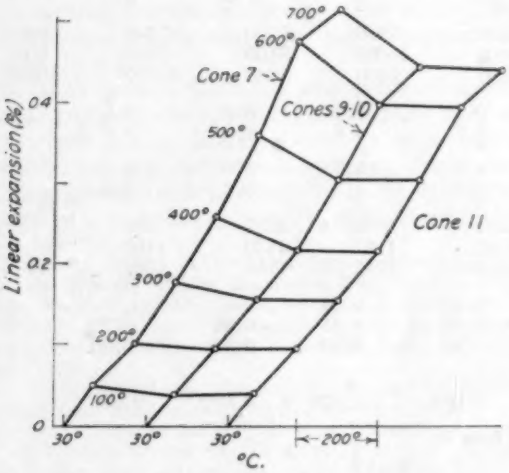

FIG. 4.—Thermal expansion of body No. 2.

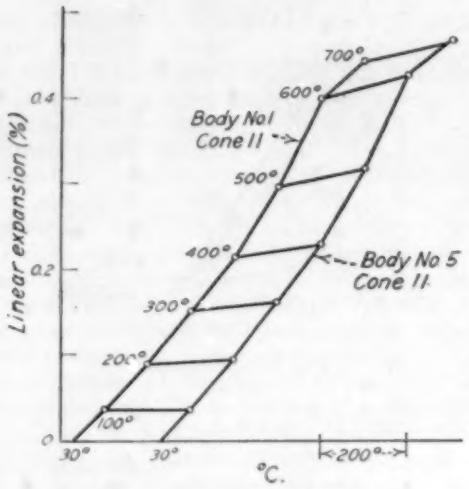

FIG. 5.—Thermal expansion of bodies Nos. 1 and 5.

Body No. 6 contained nepheline syenite as the principal flux and a reduced amount (one third) of dolomite. On the basis of the properties tested, this body looked very good, and of the bodies which were fired to cone 11, it had the highest strength.

IV. Observations

If a lower firing temperature is not desired, it is better to reduce or to eliminate the auxiliary flux rather than to use a reduced amount of nepheline syenite. Body No. 5, which had on auxiliary flux, warped less than the regular body, and it had good strength. A good hotel china body is obtained when dolomite is used with nepheline syenite and when the firing is done from two to three cones lower. If the bisque-firing temperature

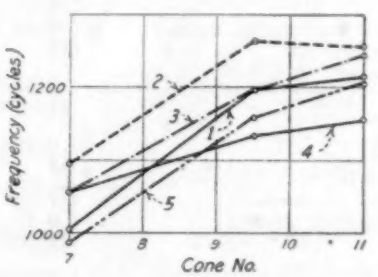

FIG. 6.—Pitch.

is lowered, however, a correspondingly lower temperature glaze is necessary, whose properties of abrasion and corrosion resistance would equal those of the present hotel china glazes.

Acknowledgment

The writer wishes to express his indebtedness to G. A. Bole for his general guidance and advice. Acknowledgment is also given to the Great Lakes Foundry Sand Company, Edgar Plastic Kaolin Company, and American Nepheline Corporation, sponsors of this investigation.

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ZIRCONIA–MAGNESIA SPINEL SYSTEM*

BY R. F. MATHER

ABSTRACT

An investigation of the zirconia–spinel system, ZrO_2–$MgAl_2O_4$, was made, using the criteria of thermal expansion, density, and microstructure. The samples were fired for six hours at 1650°C. No stable compounds or solid solutions were formed. An unstable solid solution, possibly based on a zirconia–spinel compound, was formed, however, apparently extending from pure spinel to 30 mol. % of zirconia. The solid solution gradually decomposed on repeated heating to 1300°C., and the system ultimately behaved as a series of simple aggregates of zirconia and spinel. The zirconia transformation took place at 1110°C. throughout the system. On cooling, the transformation temperature was lowered by the presence of spinel from 990°C. for the zirconia-rich samples to 630°C. at the spinel end of the system.

I. Purpose

Because of the comparative inertness of zirconia and spinel to slags, it might be expected that a valuable refractory could be formed by combining the two. A study of this system, therefore, was made.

(1) Summary of Previous Work

Cohn[1] has given the most complete account of the zirconia transformation, and he also describes the crystal structures of the same specimens.[2] Both the expansion and the crystal structure were found to vary widely with firing temperature and with impurities. The low-temperature form of zirconia is monoclinic, changing to tetragonal at about 1100°C.; a trigonal form also occurs but only in specimens fired at 2300°C. or above. When more than 4% of magnesia is present, a fluorite structure is obtained. Ruff and Ebert[3] showed this structure to consist of a solid solution of zirconia in the compound $Mg_2Zr_5O_{12}$. Similar compounds are formed between zirconia and other cubic metallic oxides when the metallic ions are smaller than the zirconium ion. Spinel has a cubic structure in which the size of the magnesium ion is about equal to that of the zirconium ion, whereas the aluminum ion is smaller. The conditions are thus present for such a compound to be formed from zirconia and spinel. No compounds occur in the zirconia–alumina system according to Ting,[4] who used the method of X rays, and according to von Wartenberg and Gurr,[5] who took the melting points of the system.

II. Preparation of Specimens

The zirconia used had 1.03% of total impurities. The spinel was produced from calcined Grecian magnesite and c.p. alumina and had 3.3% of total impurities. Test samples, which contained 0, 10, 20, 30, 40, 50, 80, and 100 mol. % of zirconia, were numbered 0, 1, 2, 3, 4, 5, 8, and 10, respectively. They were first ball milled wet for 16 hr., dried, dry pressed, and fired at 1650°C. for 3 hr. The material was crushed and sized to produce a grog yielding minimum porosity and firing shrinkage.[6] After adding 20% of unfired material, the samples were dry pressed in the form of thermal-expansion bars, 6 in. long by $1/2$ in. square, and the bars were fired for 3 hr. at 1650°C.

III. Thermal Expansion

The expansion apparatus used was similar to that described by Norton.[7] Two thermal-expansion curves for each specimen were first taken with a heating rate of 4°C. per minute. The specimens were allowed to cool with the furnace. Finally one curve for each

* Received May 20, 1941; revised copy received October 3, 1941.

[1] W. M. Cohn, "Thermal Expansion from 0° to 1400°C. of Zirconia Prepared in Different Ways," *Keram. Rundschau*, **38**, 721, 753, 777, and 784 (1930).

[2] W. M. Cohn and S. Tolksdorf, "Dependence of Structure of Zirconia on Previous Heat-Treatment," *Z. Physik. Chem.*, **8**, Abt. B, [5] 331–56 (1930); *Ceram. Abs.*, **10** [8] 604 (1931).

[3] O. Ruff and F. Ebert, "Structure of Zirconia," *Z. Anorg. Chem.*, **180**, 19–41 (1929); *Ceram. Abs.*, **8** [9] 660 (1929).

[4] Cited by O. Ruff and F. Ebert, *loc. cit.*

[5] H. von Wartenberg and W. Gurr, "Melting Points of Refractory Oxide Systems, III," *Z. Anorg. Chem.*, **196** [4] 374–83 (1931); *Ceram. Abs.*, **11** [1] 58 (1932).

[6] F. H. Norton, "Effect of Grain Sizing on Shrinkage and Porosity of Georgia Kaolin Refractories," *Bull. Amer. Ceram. Soc.*, **12** [12] 336–37 (1933).

[7] F. H. Norton, "Thermal Expansion of Refractories," *Jour. Amer. Ceram. Soc.*, **8** [12] 799–815 (1925).

specimen was taken on both heating and cooling, using a rate of 4°C. per minute throughout. Preliminary experiments showed that with this rate the temperature of the specimen did not lag behind that of the thermocouple by more than 10°C. over the range 150° to 1300°C., the latter being the maximum temperature attained on each run.

A typical heating and cooling curve is shown in Fig. 1 for specimen No. 3. Owing to thermal lag, the curve starts parallel to the temperature axis and the line becomes more or less straight up to 1100°C. Deviations from a straight line are characteristic of zirconia as well as of spinel. The temperatures at which deviations occur owing to one constituent remain unaltered by the presence of the other. Increases in the coefficient of expansion of spinel took place at 210°, 425°, 590°, 795°, and 1080°C. and in that of zirconia at 305°, 625°, and 759°C.

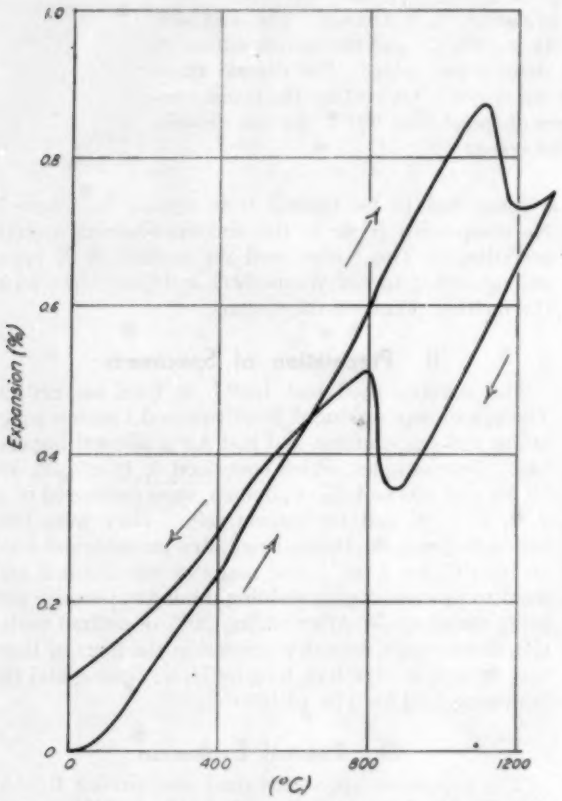

FIG. 1.—Thermal expansion of specimen No. 3, zirconia 30% and spinel 70%; third test run.

The average coefficient of expansion of spinel was 6.9×10^{-6} cm. per cm. per °C. up to 500°C., and 9.7×10^{-6} from 500° to 1300°C. The average values for zirconia were 4.9×10^{-6} up to 300°C., 7.2×10^{-6} from 300° to 800°C., and 12.5×10^{-6} from 800° to 1000°C. These results, in general, agree well with those of other observers.

On heating above 1000°C., a gradual decrease in the coefficient of expansion marked the beginning of the zirconia transformation, at 1025°C. for pure zirconia, and at 1085°C. at the spinel end of the series. The transformation temperature was progressively lowered on successive test runs. The average values for all first, second, and third runs were 1070°, 1065°, and 1055°C., respectively.

Contraction in length began at 1110°C. on almost every sample, independent of the number of expansion tests previously made. Cohn's[1] figure for zirconia fired at the same temperature is 1000°C. The temperature of maximum elongation did not depend on the impurities present in the zirconia. On two runs only was the transformation complete at 1300°C., as indicated by a reversible expansion on cooling. No accurate estimate could be made of the coefficient of expansion of the high form of zirconia.

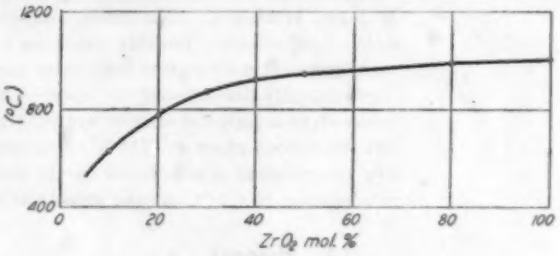

FIG. 2.—Relation between transformation temperature on cooling and molecular composition.

On cooling from 1300°C., a contraction of $9.5 \pm 0.5 \times 10^{-6}$ cm. per cm. per °C. was obtained on almost every specimen regardless of whether or not the transformation was complete. In this range, the values for zirconia and spinel were 9.1 and 9.7×10^{-6}, respectively. Reversion to the low form of zirconia took place with a certain amount of undercooling. Figure 2 shows the temperatures at which expansion began again, plotted against molecular composition. The transformation on cooling commenced abruptly and was not preceded by a gradual decrease in coefficient of expansion such as occurred on heating. The final rate of contraction down to room temperature was less than the corresponding rate of expansion (Fig. 1).

TABLE I

CHANGE IN LENGTH DUE TO ZIRCONIA TRANSFORMATION (cm./cm. $\times 10^{-3}$)

Specimen No.	Test run No. (1)	(2)	(3)	Cooling	Avg. change in zirconia vol. (%)
1	0	0.5	1.9	1.1	0.16
2	0	0.5	1.3	2.9	0.10
3	0	1.7	3.3	2.6	0.10
4	0.6	2.4	3.8	3.2	0.09
5	1.0	2.1	4.2	(1.5)	0.07
8	4.5	2.5		5.0	0.06
10	6.4	9.0	9.4	11.5	0.09

The amount of zirconia transformation may be estimated by the ordinate between the extrapolated curves before and after the transformation at its mean temperature. Values thus obtained on different tests are given in Table I.

The amount of material involved in the transformation increased with the zirconia content and with the number of runs previously made on the specimen. In four cases out of seven, the average change in length was proportional to the volume of the zirconia. For those samples, the average linear change of the zirconia was 0.95% or 2.85% by volume. The volumes of the monoclinic and tetragonal unit cells, according to Ruff and Ebert,[3] are 142.7 and 133.0 cubic a. u., respectively, giving a linear change on transformation of 2.26% or 6.78% by volume.

A net increase in length was generally observed at the end of a test run. This expansion, which apparently was due to the formation of spalling cracks, was greatest in the specimens of high zirconia content and of low porosity. The true net change in length, therefore, could not be measured, and the change in length at the transformation was probably also affected.

IV. True Density

After the thermal-expansion measurements had been completed, a sample was taken from each bar to determine its true density. The results in Fig. 3 show that there is a linear relation between specific volume and composition by weight, as would be expected of a series of conglomerates. Although density measurements indicate clearly that there are no compounds, they are not so conclusive in showing the absence of solid solutions because these are formed from their constituents with little change in volume.

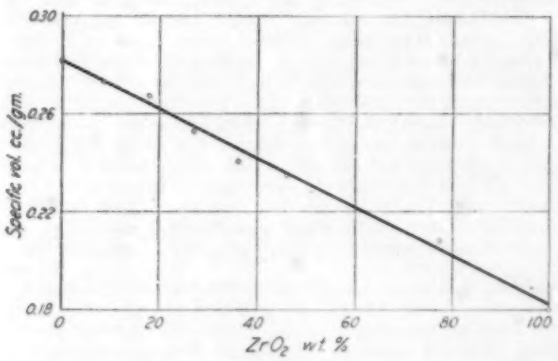

FIG. 3.—Relation between specific volume and composition by weight.

From the mean specific volume curve, the density of pure zirconia was found to be 5.51 gm. per cc. Cohn's[1] values for the monoclinic form range from 5.16 to 5.81, with an average of about 5.4 gm. per cc. The X-ray measurements of Ruff and Ebert[2] give the density of the monoclinic form as 5.70 gm. per cc.

V. Microstructure

Thin sections and powder samples of 100-mesh were also made from the specimens at the conclusion of the expansion measurements. Figure 4 shows the microstructure of specimen No. 2. There was some difficulty in obtaining good thin sections because of the low cohesion of the material, particularly in the zirconia-rich samples.

The formation of spinel was complete, however, in all samples. Spinel is isotropic and has a refractive index of 1.72, whereas monoclinic zirconia is anisotropic and has a mean refractive index of 2.17. The two substances may therefore be readily distinguished under the microscope. No quantitative estimate of the relative amounts of the two oxides could be made. The pure zirconia showed only anisotropic material, indicating that the cubic material was not obtained. The crystals were too small to give interference figures, and it was therefore impossible to say whether any of the tetragonal form was undercooled to room temperature. The crystallization of the zirconia and of the spinel was noticeably affected by the presence of the other constituent, causing smaller crystals to be formed. The effect was particularly marked in the case of spinel.

VI. Discussion of Results

The measurements of thermal expansion provide conclusive evidence that no stable compounds or solid solutions are formed in the zirconia–spinel system, and this evidence is supported by determinations of density and microstructure. Table I shows that a compound or solid solution is formed at the spinel end of the system, which gradually decomposes on repeated heating and cooling, as shown by the increasing amount of zirconia which undergoes transformation at 1100°C. Samples that contain less than 40% of zirconia do not show any material transforming on the first expansion run, but the limits of solid solubility may be greater than this owing to some decomposition on the initial cooling after firing. The pure zirconia sample itself shows a greater amount of material transforming on the second run than on the first, presumably due to the 1% of impurities it contains. Further evidence of the interaction of the zirconia and spinel is the increase of undercooling with spinel content. Undercooling may be due principally to impurities dissolved in the zirconia, the

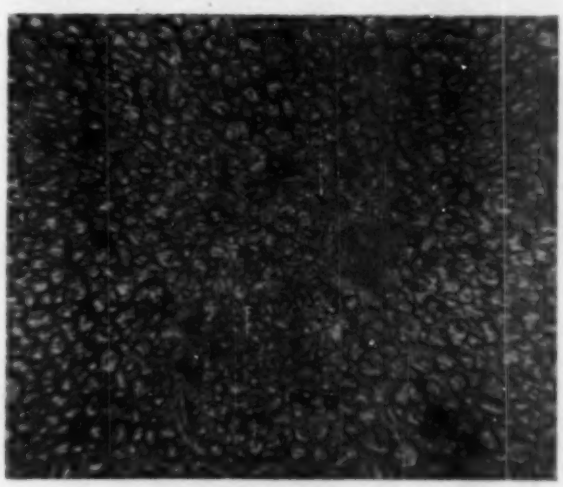

FIG. 4.—Structure of specimen No. 2, zirconia 20% spinel 80%; ×200.

amount being largest in the spinel-rich samples, resulting either from greater diffusion or from a less complete breakdown of the solid solution.

The point at which contraction begins on heating is taken as the transformation temperature, namely, 1110°C. The constancy of this figure throughout the system indicates that there is little, if any, superheating, in contrast to the large amount of undercooling obtained. This is in accordance with the general rule that superheating is more difficult to produce than undercooling. The hysteresis is a measure of the amount of change in structure involved in the transformation. Because the positions of the atoms in the monoclinic and tetragonal unit cells have not been determined, it is not possible to estimate the degree of change in structure. From the hysteresis, it appears to be intermediate between the sluggish and the high-low inversions of quartz, though closer to the latter in which the change in energy is small. The gradual decrease in coefficient of expansion which precedes the transformation on heating is contrasted by the abrupt beginning of the transformation on cooling. Benedicks[8] suggests that the high form is soluble in the low form, whereas the low form is insoluble in the high form.

It is possible that, under other conditions, a stable compound or solid solution can be formed in the zirconia–spinel system by the use of higher firing temperatures, of mineralizers, or of more reactive forms of the materials. The nature and stability of such a compound or solid solution may be studied by means of X rays as well as by the methods of thermal expansion, density, and microstructure.

[8] C. Benedicks, "Allotropy in General and That of Iron in Particular," *Jour. Iron and Steel Inst.*, **86**, 242–71 (1912).

Acknowledgment

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February 1, 1942
21—2

Abrasives

Effects of surface finish. J. T. BURWELL, J. KAYE, D. W. VAN NYMEGEN, AND D. A. MORGAN. *Jour. Applied Mechanics*, **8**, 49–58 (1941); *Chem. Abs.*, **35**, 5830 (1941).—Various surface finishes were tested on steel shafts. The finish has very little effect on the operation of a journal bearing in the region of hydrodynamic lubrication but affects the load capacity. The KCNS test for Fe was used to measure the actual quantity of Fe worn off. Actually, very little metal is removed during the running in of a journal bearing. The oil on the bearing after its operation was refluxed with aqueous acid solution, and the layers of oil and dilute acid were separated. In the latter, the Fe^{++} was oxidized, and the solution was tested with KCNS reagent. The red color was measured in a colorimeter.

Force-feed coolant system for Porter-Cable belt grinder. ANON. *Machinery* [N. Y.], **48** [3] 224 (1941).—An improved wet-belt grinding machine which may be used for surfacing operations on metals, plastics, minerals, and other materials is described. R.H.B.

Metal-polishing disks containing embedded diamond abrasive; changes in the grinding surface during polishing. E. KLÜPPELBERG. *Werkstatt & Betrieb*, **72** [23–24] 300–304 (1939); *Met. Abs.* (Inst. Metals), **7** [7] 320 (1940).—The influence of the principal factors in the efficiency of polishing disks has been investigated by Kruel; several of his conclusions are examined and are amplified by evidence obtained from microexamination of materials and abrasives and of the disk at various stages in the grinding process. Conclusions are reached regarding the optimum particle size of the abrasive, the orientation of abrasive particles as grinding proceeds, and the modifications which occur in the surface of the disk.

Pacific Vera-Lathe for polishing, lapping, and buffing. ANON. *Machinery* [N. Y.], **48** [3] 222 (1941).—A specially designed machine for polishing, lapping, and buffing round metal parts is described and illustrated. R.H.B.

Relative mechanical corrosion hardness of synthetic corundum and other minerals. W. FR. EPPLER. *Zentr. Mineral., Geol.*, **1941A**, 73–85; *Chem. Abs.*, **35**, 5417 (1941).—The relative mechanical corrosion hardness (I) is defined as the density divided by the loss in weight in gm. per sq. cm. exposed surface when the substance is sandblasted in a special apparatus under standard conditions. Corundum grains were used as corroding agent. Eight samples of synthetic corundum gave practically identical results, which were not affected by previous heat-treatment of the samples at 800° for 72 hr. Values of I for other minerals were as follows: talc 1.06, gypsum 1.05, calcite 1.72, fluorite 1.69, apatite 0.85, orthoclase $\perp$ acute bisectrix 8.56, $\parallel$ acute bisectrix 7.12, quartz 17.0, topaz $\perp$(001) 12.0, $\parallel$ (001) 15.4, synthetic corundum $\parallel$ *c* axis 117, $\perp$ *c* axis 85, and diamond 1853. These results are compared with the values for scratch and grind hardness. There are notable differences; the low result for apatite and the greater hardness of quartz than that of topaz are astonishing. Other materials examined gave the following values: synthetic resin (trolon) 24, eraser rubber 222, copper 239, cast iron 274, brass 441, tire rubber 585, and silver steel 645. It is evident that I is a function not only of the hardness but also of the elastic properties of the substance.

PATENTS

Abrading machine. J. B. HADAWAY (United Shoe Machinery Corp.). U. S. 2,262,801, Nov. 18, 1941 (Sept. 22, 1939).

Abrading tool. J. A. CARLIN AND C. W. FLOSS (Honing Equipment Corp.). U. S. 2,264,360, Dec. 2, 1941 (Aug. 14, 1939).

Abrasive and polishing wheel. STEPHEN WARREN LIPITT. Ger. 701,398, Dec. 12, 1940; 67*a*. 1; *Chem. Abs.*, **35**, 8234 (1941).—The polishing wheel is made of several layers of yarn wound on a core, e.g., wood, and carrying the abrasive powder.

Abrasive wheel for polishing wood. MAX BÖTTGER. Ger. 701,766, Dec. 19, 1940; 55*a*. 1.31; *Chem. Abs.*, **35**, 8234 (1941).

Blade-grinding machine. W. W. HARTMAN. U. S. 2,265,600, Dec. 9, 1941 (March 15, 1940).

Buffing wheel. W. S. THOMAS. U. S. 2,263,410, Nov. 18, 1941 (July 24, 1940).

Burnishing machine. E. S. CORNELL, JR. U. S. 2,263,206, Nov. 18, 1941 (July 29, 1938).

Cylinder-grinding device. J. E. G. KLINE (Micromatic Hone Corp.). U. S. 2,263,781, Nov. 25, 1941 (Oct. 2, 1936).

Device for dressing profiled grinding wheels. SOC. GENEVOISE D'INSTRUMENTS DE PHYSIQUE. Brit. 540,588, Nov. 5, 1941 (June 24, 1939).

Encased abrasive element. J. E. KLINE (Micromatic Hone Corp.). U. S. 2,265,377, Dec. 9, 1941 (May 22, 1939).

Grinding and abrading machines. KAPELLA, LTD., AND M. H. TAYLOR. Brit. 540,299, Oct. 22, 1941 (April 10, 1940).

Grinding machine. C. G. FLYGARE AND J. I. GARSIDE (Norton Co.). U. S. 2,264,160, Nov. 25, 1941 (Nov. 4, 1939; Oct. 15, 1940). J. I. GARSICE (Norton Co.). U. S. 2,264,257, Nov. 25, 1941 (Dec. 7, 1939). W. T. SMITH AND C. M. BUIE (Allie Edgerton). U. S. 2,264,918, Dec. 2, 1941 (Feb. 21, 1940).

Grinding and polishing of flat surfaces, especially plate glass. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST.-GOBAIN, CHAUNY & CIREY. Ger. 700,900, Dec. 5, 1940; 67*a*. 15; *Chem. Abs.*, **35**, 7674 (1941).—Equipment and procedure are described.

Honing machine. A. M. JOHNSON (Barnes Drill Co.). U. S. 2,263,878, Nov. 25, 1941 (Jan. 6, 1939). G. F. JOHNSON (Bower Roller Bearing Co.). U. S. 2,264,179, Nov. 25, 1941 (Sept. 25, 1939).

Lapping machine. H. S. INDGE (Norton Co.). U. S. 2,264,163, Nov. 25, 1941 (May 3, 1941). LOUIS MALKOVSKY (Sperry Gyroscope Co., Inc.). U. S. 2,263,927, Nov. 25, 1941 (Nov. 30, 1939).

Machine for grinding the runners of skates, etc. JOHAN ÖSTBLAD. U. S. 2,264,676, Dec. 2, 1941 (Oct. 28, 1939).

Precision grinding machine. A. J. DEVLIN. U. S. 2,264,302, Dec. 2, 1941 (May 8, 1940).

Valve-grinding tool. R. A. DOUGHERTY. U. S. 2,265,130, Dec. 9, 1941 (July 21, 1941).

Variable pressure honing tool and method. K. W. CONNOR AND J. E. KLINE (Micromatic Hone Corp.). U. S. 2,265,800, Dec. 9, 1941 (Nov. 18, 1938).

Art and Archeology

Glass factories of Alsace-Lorraine before the outbreak of the French Revolution. OTTO VOGEL. *Glashütte*, **71** [17] 244–45; [18] 257–60 (1941).—V. presents excerpts from the works of the Alsatian Baron Phillip Friedrich von Dietrich on the status of the glass industry and the location of the different glasshouses in 1785 ("Description of Mineral Deposits, Mills, etc., of Upper and Lower Alsace," Paris, 1789, and "Description of Mineral Deposits, Mills, etc., of Southern Lorraine," Paris, the Year VIII (1799)). M.V.C.

Research problems in an archeological ceramic laboratory. FREDERICK R. MATSON. *Bull. Amer. Ceram. Soc.*, **20** [12] 451–53 (1941).—6 references.

Glazed tile. CERAMIC RESEARCH LAB. YENCHING UNIV. *Chemistry* [China], **5** [1] 27 (1940).—The glazed tile used in the Peiping palaces were manufactured mostly in Men-tou-kow, in the western suburb of the city. Four local colored glazes and the tile clay were analyzed. Their formulas were as follows:

Yellow glaze	1.00 PbO	0.066 Al_2O_3, 0.080 Fe_2O_3	1.54 SiO_2
Green glaze	0.874 PbO, 0.126 CuO	0.012 Fe_2O_3	1.00 SiO_2
Blue glaze	1.00 PbO	0.117 Al_2O_3, 0.004 Fe_2O_3, 0.048 Co_2O_3	2.21 SiO_2
Purple glaze	0.804 PbO, 0.174 CaO, 0.024 CuO	0.140 Al_2O_3, 0.997 Fe_2O_3	3.03 SiO_2
Tile clay	0.217 KNaO, 0.078 MgO	0.95 Al_2O_3, 0.05 Fe_2O_3	2.84 SiO_2

Based upon the above results, experiments were made with twenty-five different glazes. The RO group was kept constant at 0.8 PbO, 0.1 K_2O, and 0.1 CaO, while the Al_2O_3 varied from 0.1 to 0.2 equivalent and the SiO_2 from 1.5 to 3.0 equivalents. The following base glaze gave the best results:

0.80 PbO, 0.08 K_2O, 0.02 Na_2O, 0.10 CaO; 0.10 Al_2O_3; 1.6 SiO_2, 0.4 B_2O_3

Batch formula			
Frit		Glaze	
Red lead	172.0	Frit	225.0
Feldspar	39.0	Red lead	68.5
Calcium carbonate	15.0	Clay	9.9
Flint	65.0	Feldspar	11.1
Boric acid	69.0	Flint	23.4
Borax	11.4	Total	337.9
Total	371.4		

To obtain green, yellow, and blue glazes, 2.8% of CuO, Fe_2O_3, and Co_2O_3 were added, respectively, to the fritted batches. M.C.L.

PATENTS

Ceramic coloring compound. HEINRICH DIEHL (Deutsche Gold- & Silber-Scheideanstalt vorm. Roessler). Ger. 698,639, Oct. 17, 1940; 80*b*. 23.03; *Chem. Abs.*, **35**, 6756 (1941).—The compound consists of BeO 3, Al_2O_3 0.4 to 7.2, Cr_2O_3 0.12 to 0.24, and SiO_2 0.3 to 2.5 mol. This pigment is green and is particularly suitable for application beneath the glaze. In making or firing in this compound, care should be taken to avoid conditions which induce the formation of chromates.

Ceramic pigment for graining. C. G. GEARY (E. I. du Pont de Nemours & Co.). U. S. 2,264,749, Dec. 2, 1941 (July 24, 1940).—An improved black ceramic graining pigment which comprises a black ceramic pigment of the copper-chrome type to which has been added a metal cyanide selected from the group which consists of cobalt, cadmium, cuprous, and zinc cyanides.

Coating glass, quartz, and ceramic surfaces with a metallic layer. HANS PULFRICH AND RICHARD MAGNER (Patent-Treuhand-Ges. für elektrische Glühlampen m.b.H.). Ger. 699,019, Oct. 24, 1940; 32*b*. 10; *Chem. Abs.*, **35**, 6755 (1941).—The powdered metal is intimately mixed with 0.1 to 4% of an oxide that will not reduce during the firing. The mixture is made into a paste, spread on the glass or ceramic surface, and fired at a temperature below the melting point of the metal. Suitable oxides are boric, phosphoric, and silicic oxides or ZrO_2.

Decalcomania paper. JOHN MACLAURIN. Can. 400,201, Oct. 28, 1941 (June 26, 1940; in U. S. Aug. 11, 1939). G.M.H.

Designs for:

Floral container. R. M. KOCH. U. S. 130,691, Dec. 9, 1941 (Feb. 12, 1941).

Glass goblet. T. C. HEISEY (A. H. Heisey & Co.). U. S. 130,432, Nov. 18, 1941 (Sept. 12, 1941).

Glass mixing bowl. BELLE KOGAN (Federal Glass Co.). U. S. 130,743, Dec. 16, 1941 (Oct. 15, 1941).

Handled cup. C. J. UHRMANN (Imperial Glass Corp.). U. S. 130,486, Nov. 25, 1941 (May 24, 1941).

Hollow glass building block. R. C. KENDALL (Owens-Illinois Glass Co.). U. S. 130,518 to 130,521, Nov. 25, 1941 (March 8, 1941).

Jar. N. F. STEUER (Owens-Illinois Pacific Coast Co.). U. S. 130,605, Dec. 2, 1941 (Oct. 22, 1941).

Milk bottle. W. C. TEUNISZ. U. S. 130,689, Dec. 9, 1941 (April 19, 1941).

Pitcher. F. L. THORLEY (Copeland & Thompson, Inc.). U. S. 130,618, Dec. 2, 1941 (Aug. 20, 1941).

Vase. E. W. FUERST AND C. W. SAWYER (Libbey Glass Co.). U. S. 130,580, Dec. 2, 1941 (Sept. 25, 1941). R. B. PARSIL, JR. (Libbey Glass Co.). U. S. 130,584 to 130,586, Dec. 2, 1941 (Sept. 25, 1941). C. W. SAWYER (Libbey Glass Co.). U. S. 130,587 and 130,588, Dec. 2, 1941 (Sept. 25, 1941).

Water-closet bowl. ADOLPH HOFFMAN (General Ceramics Co.). U. S. 130,581, Dec. 2, 1941 (June 30, 1941).

Cements

Investigating the causes of the reduced dissolving out of lime in pozzuolana Portland cement mortars. I. D. ZAPOROZHETS. *Trudy Leningrad. Ind. Inst.*, No. 7 [Fiz. Mat., No. 4], pp. 63–85 (1937); abstracted in *Chem. Zentr.*, **1940, II,** 3533–34.—The behavior of pozzuolana Portland cements in fresh water is discussed under the following headings: (1) Dissolving out of lime by the filtration of water through test pieces; (2) Reciprocal action between hydraulic bonding agents and lime; and (3) Density of mortars of different cements. The materials tested were (*a*) high quality Portland cement, (*b*) pozzuolana Portland cement with 33% Si material, (*c*) pozzuolana Portland cement with 45% Bryansk kieselguhr; and (*d*) a cement made with 70% Karadag trass. The stability of pozzuolana Portland cements with regard to the dissolving out of lime was found to be much greater than that of Portland cement. The amount of lime dissolved diminished with the age of the test piece converted by an uninterrupted filtration. The reciprocal action between the SiO_2 of the admixtures and the lime produces a reaction which is a combination of an adsorption and a chemical reaction; the speed of the reaction is conditioned to a large extent by the adsorption capacity of the admixtures. The monocalcium silicate formed in this case is capable of adsorbing lime. The maximum concentration of lime in aqueous monocalcium silicate was 0.09 gm. per liter. It was determined that the continued lessening of the water solubility of the free lime in pozzuolana Portland cements is the result of chemical combining and increasing density of the mortar. M.V.C.

Magnesia cements with hydroxide gels. A. C. VOURNAZOS. *Angew. Chem.*, **53** [13–14] 136–39 (1940).—Hard hydraulic magnesia cements can be made from fired magnesite and $Mg(OH)_2$ gel prepared either by precipitation from sulfate solution or by heating MgO and water on a water bath. $Fe(OH)_3$ and $Al(OH)_3$ gels behave similarly, the latter being capable of bonding a wide variety of materials. The setting of Sorel cement is ascribed to the solution of MgO in the chloride solution with the eventual formation of the hydraulic hard-setting $Mg(OH)_2$ mortar. R.L.G.

Quaternary system CaO–SiO_2–Al_2O_3–Fe_2O_3 and its applications. QUIRINO SESTINI. *Chimica & Industria*, **23,** 163–72 (1941); *Chem. Abs.*, **35,** 6757 (1941).—Recent studies on cements are reviewed, and the graphical (tetrahedral) representations of the cement constitution are illustrated. The moduli formerly employed to indicate the changes in the properties of the cements are criticized, and new ones are proposed: (1) silicate modulus, i.e., the ratio of Ca silicates to liquid phase (in the melted mass), which indicates the "final" hydraulicity of the cement, while the former lime modulus indicated the "initial" hydraulicity; and (2) the ratio Al_2O_3/Fe_2O_3, which indicates the degree of chemical resistance of the cements. A new graphical system is proposed to represent the quaternary system on the plane (Fenaroli, *Ind. Ital. Cemento*, **1929,** No. 10).

PATENTS

Cementing material. C. A. MEEK (Resistall Corp.). U. S. 2,265,665, Dec. 9, 1941 (March 26, 1938).—A hydraulic cement obtained by finely grinding a clinker resulting from the semifusion of an intimate mixture of lime and substantially pure antigorite.

Gypsum plaster. M. C. DAILEY (Canadian Gypsum Co., Ltd.). Can. 400,229, Oct. 28, 1941 (Oct. 21, 1938; in U. S. Oct. 30, 1937). G.M.H.

Enamel

Alumina in enamels. VIELHABER. *Emailwaren-Ind.*, **17** [27–28] 73–74 (1940).—Alumina introduced as feldspar opacifies enamels to a certain extent, but too much gives a mat enamel because the alumina separates out during cooling; the slower the cooling, the more mat is the enamel. If a high borax content as well as the alumina is present, a clear enamel will be produced because of the fluxing action of the borax. Alumina is also present in mill clay, which is a cheap opacifier but requires other substances with it to give good opacification. The change from glossy to mat enamel is so sudden when alumina is used as opacifier and opacification in this case depends so much on the cooling process that it is not recommended except where a mat enamel is required. A parent batch formula for a mat enamel, such as a cast ground enamel, contains 60 feldspar, 32 Sioglur, 18 soda, 40 alumina hydrate, 12 fluorspar, 10 cryolite, 6 saltpeter, and 20 sodium fluosilicate. M.V.C.

Amount of hydrogen absorbed in steel by pickling. T. UNOTORO. *Tetsu to Hagane*, **26,** 699–702 (Sept. 25, 1940); *Jour. Iron & Steel Inst.* [London], **143** [1] 175A (1941).—U. investigated the amount of hydrogen absorbed by steel during the process of pickling and, in particular, the influence of the pickling time, the acid concentration, and the temperature of the bath upon the absorption. Experiments on specimens of 0.3, 0.7, and 0.9% carbon steels showed that (1) the amount of hydrogen absorbed increases with the pickling time, but the rate of absorption gradually decreases; (2) the higher the temperature of the bath, the greater is the amount of hydrogen absorbed; (3) when the bath temperature is 53 °C., the absorption increases with the acid concentration, but at 70 °C. there is scarcely any difference in the absorption at concentrations of 10% and 20%; and (4) the ratio of the amount of hydrogen absorbed to that evolved decreases rapidly after the first few minutes.

Automatic enameling furnace designed for controlled-oxidation firing. W. G. MARTIN. *Bull. Amer. Ceram. Soc.*, **20** [12] 430–34 (1941).—5 figures.

Changes occurring in a cleaner bath during use. J. M. ZANDER. *Bull. Amer. Ceram. Soc.*, **20** [12] 434–37 (1941).—8 figures.

Conserving the adherence oxides cobalt and nickel in enamels. H. LANG. *Keram. Rundschau*, **48** [22] 181–83 (1940).—L. discusses the possibilities of substituting other oxides or materials for Co and Ni oxides which are used in ground enamels because of their whiteness and mainly because of their firm adherence to steel sheets. The adherence of MnO equals that of Co oxide; because of its oxidizing action, MnO can replace Co oxide or at least reduce considerably the amount required. A white or very light ground was obtained with the following frits:

	Original	No. 1 on 100	Boron free	Original	No. 2 on 100	Boron free
Borax	34.0	32.70		20	19.23	
Glass powder			30			25
Quartz	23	22.12	20	31	29.81	25
Feldspar	27	25.95	26	23	22.12	20
Soda	9	8.65	12	7	6.73	7
Saltpeter	3	2.88	3	2	1.92	2
Fluorspar	4	3.85	5	15	14.42	15
Magnesia				2	1.92	2
Product F	4	3.85	4	4	3.85	4

Mill addition: 80 kgm. frit No. 1, 20 kgm. frit No. 2, 10 kgm. quartz, 7 kgm. clay, and 5 kgm. product "F" which is a mixture of barium peroxide and antimony oxide, the ratio of which is not given. The adherence is better, the darker the material after firing; the material should therefore be fired long and intensely in an oxidizing atmosphere (fresh air must be continually supplied). The adherence of these frits is considerably improved by the production, before firing, of iron oxide film on the sheet, e.g., by wiping the steel sheet with turpentine and annealing it to blue heat. Instead of MnO, fluorides up to 10 and 15% will replace Co and Ni to a great extent, especially in B-free enamels. Co and Ni oxides can also be conserved by reducing the thickness of the ground enamel layer, e.g., from 400 to 200 gm. per $m.^2$; this can readily be done with colored enamels but not with white enamels as the layer is not as uniform as is necessary. M.H.

Controlling costs in the enameling plant. FRED DOERING. *Better Enameling*, **12** [10] 11–14 (1941).—D. presents a method of maintaining a cost-control system. B.C.R.

Difficulties of preparing boron-free wet enamels. H. LANG. *Glashütte*, **71** [16] 229–31 (1941).—L. discusses the chemical reactions and changes which take place in the enamel slip, their effect on the properties of the enamel and preparation of the slip, and the effect of fineness of grinding, composition, temperature, and aging after grinding. Measures for promoting favorable reactions to obtain the optimal properties and working conditions for the enamel are suggested. With most enamels, water added to the mill dissolves out certain substances, especially alkalis and water-soluble silicates and salts, so that the wet slip always has an alkaline reaction. Further dissolving and chemical and colloidal reactions take place during the aging. That a knowledge of these factors is necessary becomes especially evident in the case of enamels with little or no borax content, where working conditions are much more difficult. It is important to know to what extent the enamel is attacked by the water in the mill, the nature of the reactions taking place, and the effect of standing or aging. Some boron-free enamels do not dissolve out in the water of the slip and behave differently from ordinary enamels. The production of boron-free enamels may be facilitated in some instances and defects minimized by the addition of suspension agents to the slip, by keeping the slip and objects to be enameled warm, especially in cold weather, and by careful drying (not too rapid or hot). Streaks in boron-free enamels can be reduced to some extent by not grinding the enamel too fine. M.V.C.

Effect of iron oxide on tensile strength of porcelain enamel. A. M. JOHNSEN AND J. J. CANFIELD. *Jour. Amer. Ceram. Soc.*, **25** [1] 29–32 (1942).—7 references, 14 figures.

Firing sheet ground enamels. ANON. *Emailwaren-Ind.*, **17** [25–26] 67–68; [27–28] 74–75 (1940).—The preheating of furnaces and grates before introducing the enameled pieces, the importance of having the degreasing baths at the right temperature after weekends and idle periods, and precautionary measures to guard against unevenness of the enamel coat are discussed as aids in minimizing defects. The periodic appearance of some defects is explained. A temperature and time chart for firing enamels of three different thicknesses has been worked out by the Porcelain Enamel & Mfg. Co. Differences which new and more efficient types of furnaces and automatic control of firing temperatures have made in older firing methods are pointed out. M.V.C.

Glass powder as substitute for borax in enamel. H. LANG. *Keram. Rundschau*, **48** [17] 142–43; [18] 151–53 (1940).—Although glass powder has long been known as a material for enamel, it has found little application. The scarcity of borax in Germany, however, necessitated the search for substitutes, and recent investigations of L. show that glass powder has the following advantages: (1) It does not burn away and is therefore fully utilized, thus making the enamel cheaper. (2) Because it is melted twice, it has a favorable influence on the expansion and elasticity of enamel and increases its resistance to boiling. Glass enamels are very acid resistant. The content of Na in the glass powder is very important, however, as Na glasses usually devitrify more easily than K glasses; formerly, this was not always noticeable, as borax or boric acid always counteracts devitrification. White enamels and certain blue or red enamels obtain much deeper and more opaque tones when cooled slowly than when cooled quickly. The following compositions are said to give excellent enamels:

White glass powder	50.0	38.17
Feldspar	28.0	21.37
Quartz	16.0	12.21
Soda	18.0	13.74
Cryolite	10.0	7.64
Fluorspar	3.0	2.29
Saltpeter	3.0	2.29
Antimonate	3.0	2.29
	131.0	100.00

Mill addition: 2% opacifier (for ordinary purposes no opacifier is used), 6 to 8% clay, and 1% soda.

Feldspar	40	39.22
White glass powder	14	13.73
Sodium silicofluoride	14	13.73
Quartz powder	10	9.80
Kaolin	10	9.80
Na saltpeter	5	4.90
Soda	9	8.82
	102	100.00

Mill addition: 6 to 8% clay and 1% soda.
A transparent flux for all color enamels is as follows:

Glass powder	63	56.76
Soda	28	25.23
Feldspar	7	6.30
Fluorspar	7	6.30
Saltpeter	6	5.41
	111	100.00

Mill addition: 6 to 10% clay, 1% soda, and suitable color oxides.
A black enamel which can eventually be used on sheets directly, without base enamel, is as follows:

Feldspar	62	48.06
Glass powder	36	27.91
Soda	20	15.51
MnO_2	8	6.20
Nigrolan	3	2.32
	129	100.00

Mill addition: 6 to 8% clay (yellow), 1% soda, and, if necessary, black oxide.
The compositions of the glass powders used are as follows:

	Ordinary glass powder	White glass powder
SiO_2	75.10	64.88
Al_2O_3	4.30	19.56
CaO	5.60	0.36
K_2O	3.30	11.04
Na_2O	9.40	3.33
MgO	0.20	0.08
Annealing loss	2.10	0.75
	100.00	100.00

The melting of these enamels does not differ from that of ordinary borax enamels. M.H.

Hydrogen in steel and cast iron: I. C. A. ZAPFFE AND C. E. SIMS. *Metals & Alloys*, **13** [4] 444–47 (1941).—Supersaturation of hydrogen in cast iron and steel causes flakes and shatter cracks. As hydrogen was found to be the gas responsible for blistering defects in vitreous enamels, its absorption during melting, casting, annealing, and fabricating was investigated. Hydrogen may be formed, during melting, from large additions of scrap and in rainy

weather. Blistering resulted when a nitrogen-treated melt was cast in a green-sand mold, but no blistering occurred when casting was done in a dry mold. The presence of reducing gases or moisture in the furnace atmosphere during heat-treatment resulted in severe blistering and lifting during firing and chipping after firing. **II.** *Ibid.*, [5] 584–89.—Tests were made in which materials such as iron oxide, graphite, fayalite, open-hearth slag, MnO_2-FeS (1:1), and $(MnO)_2SiO_2$ were placed in drilled cavities in the steel which was then fired with ground- and cover-coat enamels. The results are discussed to show the role of hydrogen in causing blistering in enamels. Hydrogen tends to diffuse in the direction of the rolling plane and thus causes more serious blistering along the edges of sheet and plate than on the flat surface. **III.** *Ibid.*, [6] 737–42. In studying hydrogen absorption at ordinary temperatures, factors such as the effect of cold-working of the steel, temperature and concentration of pickling acid, inhibitors, cathodic electrolysis, "promoters," and rusting were investigated. The many defects in vitreous enamels are caused principally by hydrogen effusion. **IV.** *Ibid.*, 14 [1] 56–60 (1941).—The hydrogen content of cast iron may be increased markedly during melting by moisture in the atmosphere or in the rust on the scrap and during casting by moisture or hydrocarbons in the mold. Hydrogen can be removed effectively from the melt by bubbling nitrogen through it prior to casting in dry molds with the result that no blistering or pinholing occurs during enameling at 725°C. Effusion of hydrogen from steel is the principal cause of the boiling phenomena in sheet-steel enameling, and at ordinary temperatures, effusion of the same gas is the cause of the chipping and scaling phenomena. Diffusion of hydrogen in rolled steel occurs preferentially within the rolling plane. The resulting effusion at the edges of the sheet and plate aggravates defects that are common to coatings on steel. B.C.R.

Occupational enamel dermatitis. G. A. BAIBURT. *Vestnik Venerol. Dermatol.*, **1939**, No. 8, pp. 24–27; *Chem. Zentr.*, **1940, I**, 753; *Chem. Abs.*, **35**, 6753 (1941).—Analyses of aqueous extracts of various types of enamels showed an alkali content (as Na_2O) of 0.1 to 0.9, chlorides up to 0.1, Cr_2O_3 0.0019 to 0.03, B_2O_3 0 to 0.3% (depending on the method of manufacture), and Co and Ni in traces. "Patch tests" were made on the skin of various workers. The lowest percentage of positive reactions was obtained with the base enamel having additions of B. It is concluded that, above all, alkaline admixtures such as K_2CO_3 produce dermatitis, while the addition of B_2O_3 in the ratio of $Na_2O:B_2O_3 = 0.5$ to 1.0 is best for the human skin. For prophylaxis and therapy the use of a cerate ointment (having a wax base) containing 5% dermatol or of Lassar's ointment containing 1% menthol and 10% glycerol before work and washing with water containing HCl after work are recommended.

Porcelain enamel license plates. ANON. *Better Enameling*, **12** [10] 21 (1941).—Kentucky is experimenting with the use of porcelain enameled automobile license plates. Such plates are already in use in the state of Delaware. B.C.R.

Porcelain enameled hot water heating tanks. J. J. CANFIELD AND J. E. SAMS. *Better Enameling*, **12** [10] 18–21 (1941).—Chief factors in the construction of satisfactory tanks are as follows: (1) a design that permits easy inspection both before and after enameling, prevents flexure due to breathing of the tank resulting from changes in pressure, and eliminates sharp radii, crevices, and sharp metal tips on corner welds; (2) perfect coverage, which can be accomplished only with two or more coats; and (3) use of an enamel having adequate resistance to hot water. 6 illustrations. B.C.R.

Use of stannous chloride as a pickling inhibitor. T. P. HOAR AND S. BAIER. *Sheet Metal Ind.*, **14**, 947–48 (Sept., 1940); *Jour. Iron & Steel Inst.* [London], **143** [1] 20A (1941).—Results are given of a series of tests with pickling baths containing, as a pickling solution, 7% (by weight) of sulfuric acid at 80°C. to which different inhibitors were added. The experiments were made to determine (*a*) the inhibitory power of stannous chloride as compared with other inhibitors, (*b*) the comparative rate of deterioration of the bath when in use and while standing idle, (*c*) the possibility of regenerating the spent bath, and (*d*) the possibility of using materials other than flour to reduce the amount of hydrogen taken up by the steel. The data obtained with 15 different inhibitors are compared in a table. The most satisfactory bath inhibited with stannous chloride contained 0.05% stannous chloride ($SnCl_2 \cdot 2H_2O$), 0.025% gelatin, and 0.05% cresolsulfonic acid. The gelatin gave a cleaner solution and better inhibition than the flour originally proposed, and the cresolsulfonic acid prevented oxidation.

PATENTS

Black enamels and glazes. ADOLF DIETZEL AND RICHARD BONCKE (Kaiser-Wilhelm-Institut für Silikatforschung). Ger. 702,057, Jan. 2, 1941; 48*c*. 2.01; *Chem. Abs.*, **35**, 8234 (1941).—The Al_2O_3 content of the black enamels and glazes, which contain TiO_2 and the usual colored oxides, is kept below 7.5%.

Connection for glass-lined tanks. W. G. MARTIN AND J. H. CRIDER (A. O. Smith Corp.). U. S. 2,266,611, Dec. 16, 1941 (May 18, 1940).

Enameled-tank connection. W. G. MARTIN (A. O. Smith Corp.). U. S. 2,266,609, Dec. 16, 1941 (May 18, 1940).

Hot water tank connection. W. G. MARTIN (A. O. Smith Corp.). U. S. 2,266,610, Dec. 16, 1941 (May 18, 1940).

Glass

Antisplinter coatings for glass: I. O. PETZOLD. *Oil & Colour Trades Jour.*, **98**, 144–45 (1940).—The special requirements of such coatings are outlined and discussed. **II.** *Ibid.*, pp. 180–84.—Apparatus for testing the efficiency of the films, including the automatic hammer, the falling sphere, and the pendulum system, are described in detail. **III.** *Ibid.*, pp. 259–60.—Rapidly evaporating solvents should be avoided, as these cause cooling of the air surrounding the film, with consequent deposition of moisture to the detriment of the coating; excess of high-boiling solvents should also be avoided, as these cause "cold flow" and tackiness and might carry away plasticizer during evaporation. Other factors regarding solvent retention are discussed. Paraldehyde shows promise as a suitable solvent. **IV and V.** *Ibid.*, pp. 330–31, 471–72.—Requirements of plasticizers are enumerated with special reference to the effect of low temperatures, which frequently cause crystallization of these materials. Suitable plasticizers possess low volatility characteristics. Plasticizers which become yellow on aging should be avoided; materials yielding films of high moisture permeability are also undesirable. **VI.** *Ibid.*, pp. 611, 613.—Apparatus for testing the efficiency of the coatings at low temperatures is described. *o*-$C_6H_4(CO_2Bu)_2$, dimethyl*cyclo*hexyl oxalate, and triacetin used as plasticizers give good results under these conditions. **VII.** *Ibid.*, pp. 763–65; *Jour. Soc. Glass Tech.*, **25** [109] 208A (1941).—Vinyl resins, ethylcellulose, cellulose acetate, and rubber latex are discussed as being suitable materials for the coatings. The use of cellophane and textile netting is described with photographs.

Calculation of relaxation constants from tension experiments on sodium silicate glasses according to the measurements of Taylor and Dear. H. RÖTGER. *Z. Physik. Chem.*, **B48**, 108–13 (1940).—The equation for the elongation of constantly loaded glass fibers, as determined by Taylor and Dear (*Jour. Amer. Ceram. Soc.*, **20** [9] 296–304 (1937)) for Na_2O-SiO_2 glasses, is of a form which would indicate the simultaneous occurrence of two cohesion processes. On this basis, the constants of this equation are transformed into partial relaxation velocities and partial

elastic moduli characterizing each process. A tabulation of these partial quantities, calculated directly from the experimental data of Taylor and Dear, shows that (1) the relaxation velocities (γ_1 and γ_2) differ by a factor of 3 to 5, indicating that solidification occurs in several stages; (2) the elastic moduli (E_1 and E_2) are of the same order of magnitude; (3) the partial elastic modulus (E_2) of the more rapid process decreases with increasing temperature, while E_1 remains substantially constant; and (4) the viscosity ($\eta = \eta_1 + \eta_2$) is essentially determined by the slower component (η_1). The modification of the method to include the time and characteristics of instantaneous elongation is desirable but does not affect the results appreciably.

R.L.G.

Colored glass—red color: I. Bruno Schweig. *Glass*, **18** [8] 230–32, 243 (1941).—Glasses may be colored by (1) the colored atoms of metals or metal oxides present in true solution, in an ionic state, or in actual combination as a silicate; (2) groups of molecules corresponding to the chromophoric groups of organic dyes; (3) a colloidal distribution of metals or particles of other elements; (4) microscopic or ultramicroscopic colored crystals. The first is accomplished solely through the composition of the batch, while the others are dependent on the heat treatment given the glass. S. discusses batch compositions for gold-ruby and selenium-red glass. **II.** *Ibid.*, [9] 260–62, 265, 268.—S. discusses recent developments in the production of gold-ruby and copper-ruby glass. Batch compositions for red selenium glass with and without cadmium and ruby glasses with coloring agents such as tellurium, nickel, uranium, neodymium, and erbium are given. **Yellow color: I.** *Ibid.*, [10] 286–91.—S. discusses the use of yellow coloring materials used in the production of yellow and amber glasses. The coloring effects of sulfur together with the contradictory views as to the essential form, i.e., sulfide or element, are mentioned briefly. Inorganic cyanogen compounds are used as a source of carbon. Compositions of batches for yellow glasses containing (1) sulfur, (2) carbon, (3) sulfur and carbon, (4) FeO and MnO_2, (5) iron and arsenic, (6) cadmium sulfide, and (7) cadmium and selenium are given. Batches designed for a sharp cutoff in yellow and in orange are also given. See *Ceram. Abs.*, **20** [11] 260 (1941).

B.C.R.

High frequency electric glass welding. Contribution of electrothermics to the glass art. E. M. Guyer. *Trans. Electrochem. Soc.*, **79**, 187–98 (1941).—There is an increasing demand in the electrical industry for special glasses such as those which will withstand higher temperatures. To the glass worker, this means the faster melting of larger masses of harder glasses. As there are serious limitations in melting glass by gas and fire, faster melting of larger masses of harder glass has led to electric melting. High frequency electric glass welding has been successfully applied to the manufacture of new glassware and to the repair of glass articles broken in service. Numerous cases of electric glass welding are described. The principal advantages of electric glass welding in production operations are (1) faster melting, (2) deeper heat penetration into thick glass, and (3) more accurate control of glass temperature both along the melting line and in regions adjacent to the sealing zone.

F.G.H.

Insulation. H. Warren. *Jour. Inst. Elec. Engrs.* [London], **87**, 588–96 (1940).—W. describes insulation such as resins, glass fiber, and varnishes applied to the outside of conductors and a new method of pressing such insulation into involved shapes by steel shot. The composition of special glasses for mercury discharge lamps is given.

L.R.B.

Mixing raw materials. Zsch. *Glashütte*, **71** [22] 307–308 (1941).—Factors conditioning the thorough mixing of the batch are discussed. The grain size of the raw materials may determine the thoroughness and rate of mixing of the batch; constituents which are too coarse should not be used because they tend to become concentrated in nests. Research has shown that materials of similar specific gravity and grain size require longer mixing time. Specific weight and volume weight have a greater effect than grain size on the mixing of the batch. Heavier materials such as red lead or barium carbonate tend to sink to the bottom, and light materials remain on top; therefore, the heavier the material, the finer it should be ground. The same is true of the volume weight. It is well known that heavy soda mixes more readily than lightweight soda. The moisture content is usually introduced with the sand; if the sand is too wet, lumps will form in the mix, especially if powdered lime and feldspar are present. Very wet sand prolongs the mixing time. The optimum moisture content for thorough mixing is from 4 to 5%. If the sand and soda are mixed for a short time before other constituents are added, the formation of lumps can be entirely prevented. Other raw materials should be as dry as possible before being added. Moisture in the air may also combine with the batch constituents, especially soda, to form injurious crusts and lumps; for this reason, the air in the mixing rooms should be kept as dry as possible. The mixing time is determined mainly by the factors already mentioned, and there is a definite mixing time for every grain size, weight, and moisture content of the raw materials. For the commonest raw materials of the proper moisture content, the optimal mixing time is from 5 to 7 min., if the machine operates efficiently, but may be lengthened to 10 min. if there is much variation in weight and grain size. The fullness of the mixers also affects mixing time; the mixers will not operate efficiently if they are too full or if they are not full enough. The capacity of the machine is specified by the manufacturer and must be adhered to. The rate at which the mixing units of the machine should revolve to obtain the best results is also specified by the manufacturer and must be adhered to. A general rule for charging the mixers is to add the larger amounts first and the small additions (fining and decoloring agents) last so that the latter will be uniformly distributed.

M.V.C.

Propagation velocity of glass cracks. Anon. *Keram. Rundschau*, **48** [19] 160–61 (1940).—Cracks in glass propagate with a velocity of 1500 m. per sec., about $^1/_3$ the velocity of sound in glass. This velocity is constant irrespective of the manner in which the crack is started or its cause; the previous treatment of the glass has no effect on the velocity of propagation of the crack.

M.H.

Reaction between hydrogen and Pyrex brand glass. Lathrop E. Roberts and Clarence Bittner. *Jour. Amer. Chem. Soc.*, **63** [6] 1513–16 (1941).—When hydrogen is heated with Pyrex brand glass at an initial pressure of 700 mm. and at temperatures of 500° to 580°C., a steady drop in pressure is observed. This is not due to diffusion. The rate of pressure drop increases rapidly with temperature; at a given temperature, when hydrogen is added to restore the initial pressure, the pressure drop proceeds with diminishing rate with successive additions. No equilibrium is reached. Hydrogen recovery varies from 23.5 to 55% and is less, the higher the temperature. About 10% of the hydrogen which disappeared is accounted for as water. The glass is greatly darkened, the effect extending far below the surface. The process is interpreted as being due chiefly to an irreversible reaction rather than as adsorption. The amount of hydrogen removed is sufficient to be of importance in pyrolyses in Pyrex brand glass in which hydrogen is a product. Illustrated.

F.G.H.

Several stages in the solidification processes of silicate glasses. A. Smekal. *Z. Physik. Chem.*, **B48**, 114–18 (1940).—The experimental work of Taylor *et al.* ("Elastico-viscous . . . ," *Ceram. Abs.*, **17** [8] 273 (1938)) on glasses has been elucidated by the elaboration of the Maxwell theory to include several relaxation processes. If the partial relaxation times and partial viscosity characteristics of each process are independent of one another, they can be represented as being dependent on temperature by the Boltzmann factor, $e^{\frac{-W}{RT}}$, where W is the energy of activation. Linear relations are obtained on plotting log partial relaxation times (λ_1 and λ_2) or log partial viscosities (η_1 and η_2) against temperature for individual glasses of Taylor *et al.*, with no indication of any transformation points.

Calculating heats of activation from these, S. found that, in the temperature range of the solidification process, the relaxation time of the slower process (λ_1) possesses the greater energy of activation. The energies of activation of the slower process do not change appreciably with Na_2O content or with substitution of CaO, so that this process is concerned more directly with the SiO_4 framework. The energy of activation of the more rapid process (shorter relaxation time) decreases, however, when the Na_2O content is increased and increases when CaO is introduced. This process is thus bound up with the influence of the cations upon the surrounding SiO_4 groupings. R.L.G.

Should we protect our eyes against ultraviolet radiation? R. GUTZEIT. *Blätter Untersuch.- & Forsch. Instrumente*, 13 [2] 17–22 (1939); abstracted in *Glastech. Ber.*, 17 [8] 257 (1939); *Jour. Soc. Glass Tech.*, 25 [109] 223A (1941).—G. discusses all possible injuries inflicted by ultraviolet radiation of the sun under various climatic and geographical conditions and gives suggestions with regard to the use of Ultrasin glasses *A*, *B*, *C*, and *D*. The light transmission of glass *A* is similar to that of common spectacle glass. *B*, with a 2-mm. wall thickness, shows a transmission of 80%, *C* 50%, and *D* 30% only. The glasses differ in their color, *B* being a slight pink, *C* a grayish brown, and *D* a dark-brown color. Besides the absorption in the visible spectrum, there is another in the infrared with a steep fall at about 360 mμ. The Ultrasin glasses *A* and *B* absorb 10% of the infrared, *C* 20%, and *D* 35%, which in most cases is believed to be sufficiently effective. These protective glasses cannot be used, however, under conditions of extremely high infrared radiation, e.g., in foundries and in the vicinity of welding and melting furnaces.

Substitution of sodium phosphate for borax in the glass batch. L. SPRINGER. *Sprechsaal*, 72, 393–95 (1940); abstracted in *Chem. Zentr.*, 1941, I, 96.—Laboratory tests on lime and lead glasses and large scale production in a bottle glass factory proved that borax containing crystal water can be replaced by half the amount of $Na_4P_2O_7$; any changes which occurred in the chemical and physical properties of the glasses were not investigated. M.V.C.

Transmission of ultraviolet rays of dark-colored glass medicine bottles and jars and its measurement. S. MOSZONYI AND J. RAGETTLI. *Magyar Gyógyszerésztud. Társaság Értes.*, 15 [2] 192 (1939); abstracted in *Glastech. Ber.*, 17 [8] 258 (1939); *Jour. Soc. Glass Tech.*, 25 [109] 223A (1941).—A simple procedure was used for the determination of the ultraviolet transmission of dark-colored medicine bottles: two freshly prepared solutions (I and II*) are mixed in a proportion of 1 : 2 in such a way that the amount of the mixture constitutes one quarter of the bottle volume. After the mixture is heated at 40° to 45° in a white porcelain dish, it is subjected to the radiation of daylight or a quartz lamp, the time necessary to obtain the deepest blue coloring being determined. The solution colored behind a glass permitting total transmission is used as standard solution. The same procedure was applied to another part of the mixture poured into the glass bottle to be tested. The same conditions should prevail during radiation, with the slight modification only of placing the bottle vertical to the direction of the rays and rotating it twice in a minute. The blue solution, colored slightly weaker, was compared with the standard solution in the porcelain dish. The calculation was made according to the Beer-Lambert law, the results for the standard solution being equaled to 100. The results are given below.

	Cylindrical bottles		Flat-sided bottles	
Color of glass	Wall thickness (mm.)	Ultraviolet transmission (%)	Wall thickness (mm.)	Ultraviolet transmission (%)
Colorless	2.21	27.5–30.0	2.44	21.5–25.0
Light green	2.33	37.5–41.2	1.72	42.5–43.5
Dark green	1.82	20.0–21.2	3.05	18.7
Light brown	0.97	35.0	0.78	60.0–62.5
Brown	1.27	13.7–15.0	1.38	26.2–27.5
Reddish brown	1.82	15.0–16.2	1.25	16.2
Rusty brown	2.28	11.2–13.7	1.98	12.5–15.0

* Solution I consisted of an aqueous solution of the tartrate of the alkaloid of the fungus of ergot, isolated according to the prescription of the British Pharmacopoeia. Ergotoxinaethanosulfate (0.0125 gm.) and tartaric acid (1 gm.) dissolved in distilled water (100 cc.) were preferable. Solution II consisted of a solution of 0.125% *p*-dimethylamidobenzaldehyde in sulfuric acid of 50%. After 24 hr., the solution was ready for use; it can be kept 6 days.

Tin in glass manufacture. ANON. *Engineering*, 152 [3943] 104 (1941).—The use of tin oxide as an opacifier is discussed briefly. B.C.R.

ζ-potential of glasses of various compositions. BÉLA VON LENGYEL AND JÁNOS VINCZE. *Magyar Chem. Folyóirat*, 47, 20–24 (1941); *Chem. Abs.*, 35, 5659 (1941).—The glasses investigated contained, in mol. %, (1) SiO_2 72, Na_2O 22, and CaO 6, (2) SiO_2 60, Na_2O 24, and CaO 16, (3) SiO_2 75, B_2O_3 11, Al_2O_3 3, and Na_2O 11, and (4) SiO_2 72, B_2O_3 14, and Na_2O 14. The cataphoretic migration velocity of the single glass suspensions was measured in solutions containing various concentrations of H and Na ions. The ζ-potential was not affected by the chemical composition of the glass.

PATENTS

Apparatus for:

Bending glass sheets or plates. D. L. MCCLURE (Libbey-Owens-Ford Glass Co.). U. S. 2,263,005, Nov. 18, 1941 (July 19, 1939).

Cutting sheet glass. W. F. BROWN AND J. L. DRAKE (Libbey-Owens-Ford Glass Co.). U. S. 2,262,988, Nov. 18, 1941 (Oct. 4, 1937).

Drawing glass sheet. COMPAGNIE INTERNATIONALE POUR LA FABRICATION MÉCANIQUE DU VERRE (Procédés Libbey-Owens) Soc. ANON. Brit. 540,381, Oct. 29, 1941 (April 12, 1939).

Making glass sheets. W. O. LYTLE (Pittsburgh Plate Glass Co.). U. S. 2,264,245, Nov. 25, 1941 (July 5, 1938).

Manufacturing glass sheets. LOUIS HABERT (Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St.-Gobain, Chauny & Cirey). U. S. 2,263,493, Nov. 18, 1941 (March 17, 1937).

Shaping glass articles. W. C. WEBER (Corning Glass Works). U. S. 2,266,484, Dec. 16, 1941 (June 7, 1939).

Tempering glass. HAROLD PERRY AND A. W. GROTEFELD (Gilt Edge Safety Glass, Ltd.). U. S. 2,265,308, Dec. 9, 1941 (Aug. 23, 1937); reissue of original U. S. 2,199,511, May 7, 1940 (March 1, 1937).

Bonded fibrous product manufacture. H. W. COLLINS (Fiberglas Canada, Ltd.). Can. 400,447, Nov. 4, 1941 (June 22, 1939; in U. S. June 22, 1938). G.M.H.

Causing glass objects to enter a channel cooling kiln. H. KREISEL. Ger. 695,784, Aug. 1, 1940; 32*a*. 34; *Chem. Abs.*, 35, 5664 (1941); addition to Ger. 690,070, March 21, 1940.—Improvements in the original conveying system are described.

Control mechanism for surfacing apparatus. A. L. HARRINGTON (Pittsburgh Plate Glass Co.). U. S. 2,264,177, Nov. 25, 1941 (July 26, 1939).

Effecting the removal of scale deposits from molds employed in glass manufacture. UNITED GLASS BOTTLE MANUFACTURERS, LTD., AND T. C. MOORSHEAD, JR. Brit. 540,481, Oct. 29, 1941 (Feb. 24, 1941).

Electric glassmelting furnace. E. V. BOREL (Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St.-Gobain, Chauny & Cirey). Can. 400,745, Nov. 11, 1941 (Aug. 11, 1937). G.M.H.

Equipment for holding plate glass during tempering. JOSEF VERREET AND KURT V. STOESSER (Deutsche Libbey Owens-Ges. für maschinelle Glasherstellung A.-G.). Ger. 701,065, Dec. 5, 1940; 32*a*. 30; *Chem. Abs.*, 35, 7674 (1941).

Fiber-glass wicking. E. B. SHAND (Fiberglas Canada, Ltd.). Can. 400,448, Nov. 4, 1941 (July 28, 1939; in U. S. July 28, 1938). G.M.H.

Forebay. G. W. BATCHELL. U. S. 2,264,232, Nov. 25, 1941 (April 13, 1940).—A forebay of a glassmelting furnace.

Glass blackboard. W. O. LYTLE (Pittsburgh Plate Glass Co.). U. S. 2,264,244, Nov. 25, 1941 (June 4, 1938).

Glass building blocks grooved on the sides of thrust. HAROLD L. EASTER (Akt.-Ges. der Gerresheimer Glashüttenwerke). Ger. 695,606, Aug. 1, 1940; 37*b*. 1.03; *Chem. Abs.*, **35,** 5664 (1941).

Glass charging and pressing apparatus and method. D. E. GRAY (Corning Glass Works). U. S. 2,263,127, Nov. 18, 1941 (March 3, 1938).

Glass composition, batch therefor, and method of making. A. K. LYLE (Hartford-Empire Co.). U. S. 2,262,951, Nov. 18, 1941 (Jan. 3, 1940).—A clear, transparent, soda-lime type glass, comprising 74.5 to 80 SiO_2, 1.5 to 6 R_2O_3, 2 to 10 RO, 10 to 14.5 alkali, and 0.15 to 0.8% fluorine and a small amount of material remaining in the glass which was introduced as fining material of an oxidizing character, the glass having the properties of good chemical durability, easy melting and fining, low cost, excellent color, low checking characteristics, desirable working qualities, and excellent homogeneity.

Glass feeder control apparatus. J. R. BEERS AND W. F. BEERS (McKee Glass Co.). U. S. 2,265,414, Dec. 9, 1941 (Oct. 22, 1938).

Glass fiber sheet, felt, and mat manufacture. SACONDO MAROCCO. Can. 399,896, Oct. 7, 1941 (Nov. 20, 1939). G.M.H.

Glass furnace. J. C. KEANEY. U. S. 2,263,848, Nov. 25, 1941 (Jan. 11, 1941).

Glass with imbedded wire. JULES A. JAFFLIN (Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St.-Gobain, Chauny & Cirey). Ger. 697,970, Sept. 26, 1940; 32*a*. 22; *Chem. Abs.*, **35,** 6754 (1941). Addition to Ger. 696,146 (see following patent).

Glass with an imbedded wire net. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST.-GOBAIN, CHAUNY & CIREY. Ger. 696,146, Aug. 15, 1940; 32*a*. 22; *Chem. Abs.*, **35,** 6410 (1941).

Glass manufacture. RUDOLF SCHMIDT AND WALTER HANLEIN (Canadian General Electric Co., Ltd.). Can. 399,612, Sept. 30, 1941 (Feb. 17, 1938). G.M.H.

Glass silk tape or strip production. STANLEY PALMER (Versil, Ltd.). Can. 400,016, Oct. 14, 1941 (June 24, 1940). G.M.H.

Glass threads. F. NEUMANN. Austrian 155,702, March 10, 1939 (March 3, 1937); 32g. 25; *Jour. Soc. Glass Tech.*, **25** [109] 191A (1941).—The furnace for melting the glass is made wholly or partly of electric resistance material.

Glass tubes and rods. FRANZ SKAUPY AND GUSTAV J. WEISSENBERG. Ger. 698,180, Oct. 3, 1940; 32*a*. 35; *Chem. Abs.*, **35,** 6754 (1941); addition to Ger. 682,719 ("Producing articles . . . ," *Ceram. Abs.*, **20** [5] 116 (1941)).—Powdered quartz is mixed with a binder and formed into tubes or rods. The formed pieces may be dried or not and are then sent through the sintering, vitrifying, and annealing zones of the furnace.

Glassworking apparatus and method. D. E. GRAY, L. N. POND, AND W. C. WEBER (Corning Glass Works). U. S. 2,263,126, Nov. 18, 1941 (Aug. 12, 1938).

Heat-treatment of glass textiles. H. R. LILLIE AND E. H. LOYTTY (Owens-Corning Fiberglas Corp.). U. S. 2,263,217, Nov. 18, 1941 (June 24, 1938).—The method of making glass textile material having a high wet strength which comprises forming filaments from a glass containing up to 3% of alkali metal oxides, fabricating the filaments into a textile material, and heating the material at a temperature between 50° and 340°C. for a period of 5 to 30 min.

Holder for lenses during surface coating. D. B. MCRAE (Eastman Kodak Co.). U. S. 2,263,008, Nov. 18, 1941 (Sept. 28, 1940).

Hollow glass block making apparatus. H. H. BLAU (Corning Glass Works). Can. 399,642, Sept. 30, 1941 (Aug. 23, 1938; in U. S. Oct. 12, 1937). G.M.H.

Hollow glass building blocks. BENJAMIN F. HAZLETON, JR., AND EARL G. REDMANN (Akt.-Ges. der Gerresheimer Glashüttenwerke vorm. Ferd. Heye). Ger. 700,693, Nov. 28, 1940; 37*b*. 1.03; *Chem. Abs.*, **35,** 7673 (1941).—Within the hollow blocks are built colored glass plates. The plates are attached within the half-block by means of a drop of molten glass, and the halves are then fused. A dye is added to the mortar used in laying these blocks.

Increasing the resistance of glass to metallic vapors. MARI JOHAN DRUYVESTEYN AND NICOLAAS WARMOLTZ (Philips Patentverwaltung G.m.b.H.). Ger. 698,098, Oct. 3, 1940; 32*b*. 6,50; *Chem. Abs.*, **35,** 6754 (1941).—The glass is exposed to the metallic vapor, and the latter is allowed to attack the glass physically, whereby some of the metallic atoms become lodged in the glass. The glass is then exposed to oxidizing conditions, thereby converting the metallic atoms into oxides.

Laminated glass. F. R. CONKLIN AND C. J. MALM (Canadian Kodak Co., Ltd.). Can. 400,233, Oct. 28, 1941 (Jan. 5, 1940; in U. S. May 24, 1939). G.M.H.

Laminated nonglare unit. J. H. SHERTS AND R. A. MILLER (Pittsburgh Plate Glass Co.). U. S. 2,264,190, Nov. 25, 1941 (March 29, 1939).

Lens. G. H. AKLIN (Eastman Kodak Co.). U. S. 2,262,985, Nov. 18, 1941 (May 17, 1940).

Lens and method of producing. R. W. LEWIS. U. S. 2,263,509, Nov. 18, 1941 (March 21, 1939).

Lifting an endless sheet of glass from a molten mass. GUSTAV OPPERMANN (Deutsche Tafelglas A.-G. (Detag)). Ger. 698,508, Oct. 10, 1940; 32*a*. 23.03; *Chem. Abs.*, **35,** 6754 (1941).

Machine for gathering and feeding molten glass. H. A. ROBSON (Crown Cork & Seal Co., Inc.). U. S. 2,266,078, Dec. 16, 1941 (Jan. 26, 1937).

Machine for shaping the mouths of tubular glass articles. CHARLES EISLER. U. S. 2,266,417, Dec. 16, 1941 (Dec. 19, 1939).

Making glassware with hollow stems. CARL MARKO (Glasfabrik Weisswasser G.m.b.H.). Ger. 702,249, Jan. 2, 1941; 32*a*. 8; *Chem. Abs.*, **35,** 8230 (1941).

Manufacture of glazed ceramic bodies. G. J. BAIR (N. S. Garbisch). U. S. 2,264,499, Dec. 2, 1941 (Nov. 29, 1938).—Apparatus for forming glazed ceramic bodies from a mixture of sand and glass in finely divided form resulting from the grinding and polishing of glass plates, the apparatus comprising a preheating furnace, having a charging end and a discharging end, for heating the mixture to a temperature above that of sintering of the glass content, a press disposed adjacent to the discharging end of the preheating furnace for compacting and forming the material into bodies of a desired shape, means to move the mixture in small portions while hot from the preheating furnace to the press, a conveyer having a loading end and an unloading end, the first-mentioned end being adjacent to the press to carry the freshly formed bodies from the press, means to transfer the bodies from the press to the loading end of the conveyer, a reheating furnace enclosing the conveyer, a grid work at the unloading end of the conveyer, means for withdrawing bodies from the conveyer and depositing them upon the grid work, and means to feed glazing material upon the bodies while they are on the grid work.

Manufacturing mirrors. PEACOCK LABORATORIES, INC. Fr. 847,178, Oct. 4, 1939; *Chem. Abs.*, **35,** 5664 (1941).—A method of applying a homogeneous film of metallic Ag on mirror surfaces consists in directing toward the surface a stream of compressed air and introducing into the air current two separately prepared solutions of Ag and NH_4 nitrate and of a reducing agent containing an alkaline accelerator. The two solutions, being intimately mixed and atomized by the compressed air, react immediately with the resultant formation of a homogenous Ag film. As reducing agent, hydrazine or reducing sugar is used.

Means for toughening glass. FERDINANDO FERRÈ. U. S. 2,263,679, Nov. 25, 1941 (Nov. 2, 1937).

Method and apparatus for grinding one-piece multifocal lenses. L. G. SIMPSON (Bausch & Lomb Optical Co.). U. S. 2,264,813, Dec. 2, 1941 (Dec. 2, 1939).

Method and structure for forming containers for molten glass. P. G. WILLETTS (Hartford-Empire Co.). U. S. 2,262,826, Nov. 18, 1941 (March 2, 1936).

Mineral fibers. CLEMENS HANNEN. Ger. 695,465, July 25, 1940; 32*a*. 25; *Chem. Abs.*, **35,** 5662 (1941).—To impart to mineral fibers a fuzz, a fine dust is sprayed on the fibers while they are still hot. The dust, e.g., powdered glass, sand, asbestos, lime, chalk, or pumice, is preheated and may be mixed with a flux. To still better simulate a natural fiber, the mineral fiber can be etched by drawing it through an etching bath.

Mineral wool forming apparatus. G. T. PEARCE (Johns-Manville Corp.). U. S. 2,264,548, Dec. 2, 1941 (Sept. 3, 1937; March 30, 1940).

Molding glass and similar materials. WÜRTTEMBERGISCHE METALLWARENFABRIK. Ger. 701,732, Dec. 19, 1940; 32*a*. 8; *Chem. Abs.*, **35,** 8230 (1941).—Decorative glassware is produced by directing a jet of air or liquid on the soft, not yet solidified glass. The jet may also contain powdered or liquid pigments and dyes.

Multilayer safety glass. SIEMENS-SCHUCKERTWERKE A.-G. Ger. 698,566, Oct. 10, 1940; 39*a*. 17.50; *Chem. Abs.*, **35,** 6755 (1941).

Ornamental tile and process of manufacture. A. D. NASH (Pittsburgh Plate Glass Co.). U. S. 2,264,183, Nov. 25, 1941 (Nov. 1, 1938).

Photographic lens. C. W. FREDERICK AND M. J. HERZBERGER (Eastman Kodak Co.). U. S. 2,262,998, Nov. 18, 1941 (May 17, 1940).

Plate glass reinforced with steel wire. HEINRICH ALBERT. Ger. 701,579, Dec. 19, 1940; 32*a*. 22; *Chem. Abs.*, **35,** 8231 (1941).—The steel wires are imbedded in the glass in the usual manner. During the imbedding process the wires are under high tension, e.g., 12,000 kgm. per sq. cm., which is released only after the glass is completely solidified.

Preparing cellular glass. W. O. LYTLE (Pittsburgh Plate Glass Co.). U. S. 2,264,246, Nov. 25, 1941 (Sept. 21, 1940); reissue of original U. S. 2,237,037, April 1, 1941 (Nov. 8, 1937).

Preventing the shrinkage in sintered silica glass. GUSTAV J. WEISSENBERG AND FRANZ SKAUPY. Ger. 698,097, Oct. 3, 1940; 32*a*. 35; *Chem. Abs.*, **35,** 6754 (1941).—By careful adjustment of the particle size of the ground quartz the shrinkage is nearly eliminated.

Producing strands of glass fibers. PIERO MODIGLIANI (Owens-Corning Fiberglas Corp.). U. S. 2,265,186, Dec. 9, 1941 (March 3, 1939).

Refractory glass. MARCELLO PIRANI (Canadian General Electric Co., Ltd.). Can. 400,805, Nov. 18, 1941 (Oct. 25, 1938). G.M.H.

Safety glass. FRITZ OHL. Ger. 698,188, Oct. 3, 1940; 39*b*. 27; *Chem. Abs.*, **35,** 6755 (1941).—The middle layer is made of cellulose ester or ether films of a varying degree of esterification or etherification.

Sealing glass to ceramic bodies. KARL ETZRODT AND HANS VATTER (Siemens & Halske A.-G.). Ger. 701,054, Dec. 5, 1940; 80*b*. 23.20; *Chem. Abs.*, **35,** 7674 (1941).—The glass should have a coefficient of expansion similar to or higher than the ceramic body. During the cooling, the ceramic part is kept at a higher temperature than the glass. The thermal-expansion curves of the glass and of the ceramic should run parallel up to 300°, and only then may they deviate. An apparatus is described for making such seals.

Spray nozzle for the preparation of fibers from glass, slag, etc. GEDEON V. PAZSICZKY. Ger. 698,023, Oct. 3, 1940; 32*a*. 25; *Chem. Abs.*, **35,** 6754 (1941).

Strainless glass. MAX AUWÄRTER (W. C. Heraeus G.m.b.H.). Ger. 697,635, Sept. 19, 1940; 32*a*. 28; *Chem. Abs.*, **35,** 6755 (1941).—The glass is annealed by heating and (or) cooling it in a compartment evacuated to 1 or preferably 0.01 mm. Hg.

Television glass-metal tube manufacture. V. H. FRAENCKEL (Hygrade Sylvania Corp.). Can. 399,664, Sept. 30, 1941 (May 27, 1937; in U. S. June 1, 1936). Can. 399,665, Sept. 30, 1941 (July 11, 1938; in U. S. June 11, 1936). G.M.H.

Tempering glass. C. J. PHILLIPS (Corning Glass Works). Ger. 701,156, Dec. 5, 1940; 32*a*. 30; *Chem. Abs.*, **35,** 7673 (1941).—The heating and the subsequent quenching are carried out in baths of molten inorganic salts, and the desired temperature of the bath is regulated by the composition of the bath. A suitable heating bath is made of alkali chromates; the tempering is done in a bath of alkali chromates to which may be added other salts, and the quenching is done in molten alkali nitrates mixed with alkaline-earth nitrates or lead nitrate.

Walls built of hollow glass blocks. EDWARD B. BAKER (Patent-Treuhand-Ges. für elektrische Glühlampen m.b. H.). Ger. 702,410, Jan. 9, 1941; 37*b*. 1.03; *Chem. Abs.*, **35,** 8230 (1941).

Structural Clay Products

Efflorescences on ceramic products. WALTER MARSCHNER. *Ziegelwelt*, **70,** 317–19 (1939); abstracted in *Chem. Zentr.*, **1940, I,** 1256.—Experiments made by M. on the value of the treatment of ceramic masses with $BaCO_3$ showed that an average of 50% $BaCO_3$ is converted. Decomposition of the $BaSO_4$ formed was not observed. The brick were pure in color, which indicates an exchange of $BaCO_3$ with the sulfates. The same masses without the addition of $BaCO_3$ showed discolorations from the sulfate additions when made into brick. This was also the case when the mixes were made with water, indicating that an exchange occurs with the SO_4 salts. M.V.C.

Freezing tests on brick. O. DRÖGSLER. *Bautenschutz*, **11,** 134–45 (1940); abstracted in *Chem. Zentr.*, **1940, II,** 3243.—Freezing tests as an aid to the testing of materials should be further investigated because of conflicting opinions on the subject. The mechanical properties of dry, water-soaked, and frozen materials give criteria for judging the stability to frost. The usual test of freezing 25 times often causes damage or loss of resistance. Additional freezing periods hasten the destruction. Repeated freezing increases the saturation until the pores are filled and disintegration begins. The severe winter of 1928 to 1929 reduced the value of stored building brick considerably. Small test pieces of roofing tile and cubes of building stone were used in the tests. The transverse strength when dry and the cubic strength dry and wet (frozen) are closely and approximately rectilinearly (but varying) connected with the freezing figure. The relationship of these types of strength is disrupted, the more often the test piece is frozen. If the stability of the frozen wet cube is expressed as a fraction of the stability dry, this proportional value falls almost rectilinearly with increasing freezing figure. Further study of freezing tests made at other institutes and using different freezing apparatus and types of brick will yield similar curves. New testing devices and processes may be adopted and the number of freezing periods reduced instead of increased, as in the tests mentioned. There is no reason to discard freezing tests as useless. See "Effect . . . ," *Ceram. Abs.*, **17** [5] 184 (1938). M.V.C.

Manufacture of porous clay products. ANON. *Schweiz. Tonwaren-Ind.*, **42** [10] 4–6 (1939); abstracted in *Chem. Zentr.*, **1940, I,** 270–71.—Cells and empty spaces can be produced in clay, as in "gas concrete," by the introduction or evolution of gases. The best process consists in mixing a carbonate (dolomite, $(Ca,Mg)CO_3$) and an acid (HCl or H_2SO_4) to generate CO_2. Medium plastic clays are best suited. A tested mix consists, in parts by weight, of 100 clay, 10 gypsum, 3.5 dolomite, and 70 sulfuric acid (1%). After firing (Seger cone 4), masses which are well suited as heat- and sound-insulating material are ob-

tained. The masses are not solid enough to be used for building purposes. M.V.C.

Relation between air and water permeabilities of building brick. R. T. STULL AND PAUL V. JOHNSON. *Bull. Amer. Ceram. Soc.*, **20** [12] 443–46 (1941).—3 references, 5 figures.

PATENTS

Brick truck. R. C. HAWKINS. U. S. 2,264,527, Dec. 2, 1941 (July 27, 1940).

Interlocking brick. C. C. WHITLING. Brit. 540,561, Nov. 5, 1941 (May 14, 1940).

Masonry joint. A. J. BOHN. U. S. 2,263,914, Nov. 25, 1941 (Nov. 4, 1940).

Method and means for erecting reinforced brick or block structures. BUILDING INDUSTRIES SERVICES, LTD., AND L. W. BURRIDGE. Brit. 540,266, Oct. 22, 1941 (May 10, 1940).

Refractories

Abrasives in the role of superrefractories. HENRY C. FISHER. *Metal Progress*, **40** [2] 177–82 (1941).—F. discusses the physical properties and industrial uses as refractories of abrasives such as fused alumina, silicon carbide, and electrically fused magnesia. Special types of refractories are desirable in cases where (1) operating temperatures are especially high, (2) high heat transfer is desired, (3) mechanical abrasion is severe, (4) chemical erosion is severe, (5) nonadherence of the slag is desired, and (6) contamination of the melt must be avoided. B.C.R.

Acid refractory materials. SHOU-REN LIU. *Kuan-yeh Biweekly*, **2** [8–9] 7 (1939).—The acid refractory materials are classified into four groups, viz., fire clay, firebrick, silica, and silica brick. The selection, manufacture, and applications of each group are discussed. M.C.L.

American refractory materials can be substituted for foreign materials. OLIVER C. RALSTON. Presented at meeting of Chicago Section, American Ceramic Society, Chicago, Oct., 1941; abstracted in *Brick & Clay Record*, **99** [4] 48, 50–52 (1941).—Domestic magnesite, pinite, kyanite, topaz, and pyrophyllite are partially relieving the pinch caused by lack of imported materials. American kyanite appears to be satisfactory at 35 mesh. Mullite refractories produced from topaz have been tested in pouring spouts of metallurgical furnaces and have given satisfactory service. Magnesite is being produced from sea water and sea-water bitterns obtained from producers of salt from sea water. Flow sheets for both processes are shown. U. S. rights for producing a stabilized dead-burned magnesitic dolomite developed in Canada have been acquired by Basic Refractories, Inc. Pinite refractories have given satisfactory service in rotary enamel smelters, silver cupel furnaces, ladles for desulfurization of iron, rotary kilns and coolers, and rotary quicksilver furnaces. B.C.R.

Basic open-hearth furnace bottoms. CHESTER R. AUSTIN. *Ind. Heating*, **8** [10] 1158–62 (1941).—A brief historical sketch of the development of bottoms for the basic open-hearth process is given. The most common construction now consists of a layer of calcined grain magnesite refractory varying in thickness from 10 to 27½ in., 9 to 15 in. of magnesite and/or chrome brick, and 4½ to 20 in. of fire-clay brick. The calcined grain magnesite acts as the hearth proper for the molten-steel bath. Second quality firebrick, hard fired, can be used, as the maximum temperature to which the brick are subjected is usually less than 2100°F. The use of a plastic chrome-ore mix above the chrome brick in the bottom, with a consequent decrease in thickness of the calcined magnesite hearth, is increasing. The layer applied is usually 2½ to 6 in. thick, depending on the installation and location; it is rammed into place. Pure calcined dolomite, ground to the fineness of rice and flour, without a bonding material, is said to give good results. Quality steels have been successfully melted. The compositions of the American and foreign dolomites are compared in the following table:

Ingredient	Eastern U. S. dolomite (%)	Native Italian dolomite (%)	Native Belgian dolomite (%)
MgO	38.25	38.12	37.50
CaO	57.50	54.94	56.50
SiO_2	1.25	2.31	0.50
Fe_2O_3, Al_2O_3 } R_2O_3	1.00	3.25	1.50
Loss on ignition	2.00	0.84	2.40

M.H.

Basic slag system. R. HAY AND JAMES WHITE. *Jour. West Scot. Iron & Steel Inst.*, **48** [6] 75–81 (1941).—In the CaO–MgO–Fe_2O_3 system, melts of the following range of compositions were studied: MgO 0 to 40, CaO 10 to 50, and Fe_2O_3 30 to 60%. In depicting the ternary liquidus surface, the outstanding feature was a trough running from the CaO-MgO eutectic toward Fe_2O_3 and reaching its minimum point in the neighborhood of the eutectic in the CaO–Fe_2O_3 binary system at about 1200°C. In the system CaO–MgO–FeO, melts having the following range of compositions were used: FeO 30 to 50, CaO 10 to 50, and MgO 10 to 40%. As CaO and FeO do not form a true binary system, the phases of the system CaO–MgO–FeO were studied as a section of the quaternary system CaO–MgO–Fe–Fe_2O_3. Although materials having a composition lying in the field CaO–MgO–Fe–$2CaO \cdot Fe_2O_3$ will in general have a high melting point, they are apt to disintegrate due to hydration of the free lime present. The melting point of $2CaO \cdot Fe_2O_3$ (1436°C.) is lowered in the presence of MgO with which it forms a eutectiferous series. Additional Fe_2O_3 results in the formation of CaO–Fe_2O_3 having a melting point of 1216°C. In comparison, Fe_2O_3 and MgO form $MgO \cdot Fe_2O_3$ (melting point over 1700°C.), which can take Fe_3O_4 in solid solution without a marked decrease in the melting point. See "Slag . . . ," *Ceram. Abs.*, **20** [3] 77 (1941). B.C.R.

Catalytic mullitization of kaolinite by metallic oxide. C. W. PARMELEE AND ANTONIO R. RODRIGUEZ. *Jour. Amer. Ceram. Soc.*, **25** [1] 1–10 (1942).—34 references, 11 figures.

Chemical analyses of the refractory materials in Szechwan Province. METALLURGIC RESEARCH LAB. ECONOMIC DEPT. OF CHINA. *Kuan-yeh Biweekly*, **2** [11] 14 (1939).—The chemical analyses of various refractory materials are tabulated for both the raw materials and the finished products. M.C.L.

Constructional refractory materials containing chromium ore. K. KONOPICKY. *Stahl & Eisen*, **61**, 53–59 (Jan. 16, 1941); *Jour. Iron & Steel Inst.* [London], **143** [1] 199A (1941).—K. reviews the literature on the production and properties of chrome refractory brick and discusses the effects of the firing and the slag reactions on the properties of the chromium-ore aggregates used in their manufacture. He traces the development of different compositions of brick and their applications with reference to diagrams of the quaternary system magnesia–silica–lime–(chromium oxide + iron oxide + alumina) and discusses the causes of the failure of chrome-magnesite brick in open-hearth furnaces. 379 references.

Grog fired at low temperature. Economical production of grog block. A. MÖSER. *Sprechsaal*, **73**, 312–14 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 3243.—M. discusses the process of manufacturing grog block from low-fired grog, developed in Russia. The clay is fired only until completely dehydrated and not until shrinkage commences (500° to 800°). This low-fired grog is then worked with bonding clay by plastic shaping or the dry-press process. The block must be fired more slowly than usual because much shrinkage occurs (between 900° and 1200°, 10° temperature increase per hr.). The properties of low-fired grog block are given. M.V.C.

Insulating firebrick for kiln construction. J. D. MCCULLOUGH. *Bull. Amer. Ceram. Soc.*, **20** [12] 437–42 (1941).—4 references, 5 figures.

Johns-Manville makes insulating firebrick. ANON. *Brick & Clay Record*, **99** [5] 46, 48–50 (1941). B.C.R.

Manganese in the basic open-hearth process. S. L. Levin and V. F. Lyaus. *Teoriya & Prakt. Met.*, 11 [10–11] 37–42 (1939); *Chem. Abs.*, **35**, 5828 (1941).—The content of Mn during melting is a criterion of the proper conditions of the melting process. A high coefficient of distribution of Mn between the metal and slag (which is determined by the composition of the steel and the amount and composition of slag) is a necessary condition for the production of high-grade steel. The main condition for high-grade steel is a high temperature during the whole melting process. A decrease of Mn in the mixture to 1% does not adversely affect the conditions of desulfurization. The other factors which affect the quality of steel are the decarbonization process, oxidizing ability of slag before deoxidation, and the method of deoxidation. Optimum conditions for the production of axle steel are as follows: (1) a constant velocity of burning of C during the whole melting process of about 0.01% per min. when steam is used and 0.05 to 0.007% per min. when air is used; (2) burning of 0.8 to 1.0% C between melting and deoxidation; (3) 60 to 80 mm. fluidity of the slag, determined by the Herty viscometer; (4) preliminary deoxidation of the metal in the furnace by silicomanganese; (5) drawing of the metal at not below 1540°; and (6) the beginning of pouring at 1480° to 1500°.

Petrography of chromite-dolomite refractories. D. S. Belyankin and B. V. Ivanov. *Izvest. Akad. Nauk S.S.S.R.*, **1939**, No. 9, pp. 53–60; *Chem. Abs.*, **35**, 2688 (1941).—Petrographic examination has shown the complexity of the silicate component, which contains Cr in various stages of oxidation and Ca_2SiO_4. The solid solution of periclase contains Fe and Mn but no Cr.

Refractories. Anon. *Metal Progress*, **40** [4] 584, 594 (1941).—Recent developments in the refractories field are discussed. The life of blast-furnace linings has increased from 105,000 tons in 1880 to over 2 million tons at present. B.C.R.

Reheating furnaces for steel plants. Theodor Stassinet. *Stahl & Eisen*, **60** [37] 809–15 (1940); abstracted in *Ind. Heating*, **8** [5] 504–508, 512 (1941).—The refractory part of hearths usually consists of about four courses of firebrick, usually of second quality, on top of which the heat- and wear-resisting layer is placed. In basic hearths, this layer consists of one flat course and one edge course of magnesite brick; in pusher or roll-over furnaces, one or two flat courses or one edge course of magnesite brick is used. Sintered magnesite which has been burned in with tar or sand is occasionally used. These materials withstand the mechanical removal of slag and chilling with water. In acid hearths, the firebrick are covered with silica brick or with firestone, gravel, or even sand, which is burned in with slag. If the hearths are not ventilated, slag must not be allowed to accumulate in great depth as it destroys the hearth and breaks through. In pit furnaces with sliding covers, silica brick has been used successfully in the lower courses of side walls, but the top courses are made of coarse-grained firebrick. Ordinarily, furnace side walls are $12^1/_2$ in., thick. They are now often insulated with 5 in. of insulating material. Roofs are made of first-quality coarse-grained firebrick; as long as the furnace temperatures are below 2000°F., no difficulty arises from insulation. A special magnesite roof, insulated and subjected to severe temperature changes, stood up very well up to 2700°F. or even higher. Recently, sillimanite brick with variable porosity have been used; the porosity increases along the length of the brick. Such brick act as combined roof brick and insulation. They have given excellent service in the ceramic industry for temperatures up to 3100°F. Sprung roofs are used for spans up to 10 ft., and suspended roofs are used for spans wider than 12 ft. M.H.

Resistance of magnesite bottoms of 185-ton open-hearth furnaces. V. Dement'ev. *Stal*, **1939**, No. 12, pp. 27–31; *Teoriya & Prakt. Met.*, **12** [10] 6–9 (1940); *Jour. Iron & Steel Inst.* [London], **143** [1] 144A (1941).—The percentage of magnesia in the magnesite is a measure of the quality of a fused-on magnesite bottom of an open-hearth furnace, and experience at the Magnitogorsk Works has shown that 75% of magnesia is the optimum proportion. Further analyses showed that the main change in the composition of the furnace bottom during the period of its service was a reduction of the magnesia content. D. deals with the causes of the reduction of the stability of the bottoms. These are as follows: (1) Diffusion of admixtures into the fused-on bottom. This in turn is conditioned by the difference in the compositions of the bottom, the metal, and the slag, as well as by the temperature and porosity of the bottom. (2) The composition of the bottom and the duration of its burning-in. Ample time for burning-in should be allowed. (3) Deposits adhering to the bottom. These are caused mainly by the practice of charging lime directly onto the bottom of the furnace. The best method is to charge a layer of clean fine iron scrap which will protect the bottom from the lime and ore and will also damp out shocks during charging. If iron scrap is not available, a layer of ore is best. (4) Chemical activity of the bottom. This is partly the consequence of causes 1, 2, and 3. The impurities which find their way into the bottom, in particular ferrous oxide and manganous oxide, undergo repeated reduction and oxidation during the various stages of the open-hearth process. Statistical investigations have shown that the oxidizing action on the bottom during the time the furnace is standing empty between heats is directly connected with the time lost in repairing bottoms. The oxidizing period during the heat has a similar effect. (5) Basicity of the slag. The maximum stability of the bottom is obtained with a lime/silica ratio in the slag of 2.6. (6) Carbon content of the metal. The higher the carbon content, the lower is the melting point and the higher is the stability of the bottom.

Resistance to thermal shock of Szechwan Pao-shih. Kou-cheng Hsok. *Kuan-yeh Biweekly*, 2 [8–9] 6 (1939).—Pao-shih, a siliceous material, has been used widely in Szechwan Province as a refractory material in constructing kilns. The chemical analysis of the material is as follows: loss on ignition 2.28, SiO_2 82.39, Al_2O_3 12.47, Fe_2O_3 1.54, CaO 0.43, MgO 0.32, and KNaO 0.97%. K. found that expansion during the quartz transformations took place when the material was heated. He recommends firing of the material before use and slow heating to increase the life of the kiln. M.C.L.

Silicon carbide brick in the side walls of furnaces. Wilhelm Werner. *Deut. Zuckerind.*, **65**, 463–66 (1940); *Chem. Abs.*, **35**, 6077 (1941).—SiC brick are used in the boiler plant of the Greifenberg sugar refinery.

Specially calcined china clay used as a refractory. A. Rigby and R. A. Green. *Trans. Brit. Ceram. Soc.*, **40** [8] 319–33 (1941).—The grog obtained by the high-temperature calcination of specially selected china clays, where attention is paid to particle shape and careful grading, has a wide potential application in the ceramic industry, including refractories. The physical properties of the material are described, and experience with its application to specific types of commercial usage is described and discussed. R.A.H.

SEPARATE PUBLICATION

Low-Temperature Carbonization—Narrow Brick Retorts: II. J. Fraser Shaw. *Dept. Sci. Ind. Research, Fuel Research Tech. Paper*, No. 50. H. M. Stationery Office, London, 1939. 26 pp., 11 illustrations. Price 1s. Out of print.—Two vertical retorts, each 21 ft. 9 in. high, 6 ft. 6 in. long, and 7 in. wide at the top tapering to 11 in. at the bottom, are built in one structure. The walls of the retorts are hollow and form a series of continuous horizontal combustion chambers or flues, one above another, with a damper regulating access from each wall to the chimney. There are 11 of these flues, each 18 in. deep by $4^1/_2$ in. wide with a 15-in. opening, the whole occupying 19 ft. of the height of the retort. The top of the uppermost combustion chamber is 6 in. below the top casting. Below the bottom flue is 27 in. of brickwork incorporating an air duct. The brickwork stands on a casting from which hang the coke chamber and coke-discharging gear. Good quality tongued and grooved firebrick are used with floor tile of the usual design. The ends of the retorts are formed

of special tongued and grooved brick which allow for the 4 in. taper in the width of the retort. Each retort is heated on both of its long sides. The firebrick are lagged with 9 in. of insulating brick, the whole structure being braced with mild steel brickstays and ties. The vertical corners of the structure should be bound and protected. Ample sightholes are provided. Expansion joints must be provided in the vertical supply pipes.

The gas and air are both supplied under pressure, the gas from a holder and the air through a fan, up to 4½ in. water-gas pressure. The burners consist of a 3-in. wrought-iron T-shaped pipe, the gas rising up the upright and the air entering at one end of the horizontal part of the T through a 1-in. wrought-iron pipe tapered at its free end to ⅞-in. diameter. The other end of the horizontal part of the T (beyond the tapered air outlet) is 8 in. long; it projects about 1½ in. into the wall of the flue and is then tapered rapidly to fit an opening 2⅛ in. in diameter which extends through the 18-in. wall to the inside of the flue. The flames produced are nonluminous. In the first set of burners, additional air is supplied above the burners and also to the inlet of the second flue; thereafter, only every alternate flue is used as a combustion chamber. Usually the heat in the gases after the fifth flue is sufficient to complete carbonization; if necessary, however, the remainder of the flues can be used as combustion chambers. A chimney is needed to draw the large volume of gases downward through the flues. To prevent damage to the retort when poking or "rodding," an 8-in. vertical pipe is fixed above the top of each retort and closed with a ball seal. The charge rests on a curved grid or comb between the teeth of which rotating blades revolve and push the coke off the comb at a slow continuous rate. Any desired temperature gradient is insured by controlling the supply of air through the various chambers. When the correct adjustments have once been made, they should not be disturbed. An excess of air will cause the lower chambers to become hotter. A decrease in gas will slightly increase the temperature of the upper chambers and will cause that of the lower chambers to fall. An increase in air pressure will have a similar effect.

A temperature of 650°C. on the inner face of the retort from top to bottom will produce a charge uniformly carbonized through to the center. Higher temperatures cause overcarbonization and produce gray coke. The optimum temperature in the first combustion chamber is 1120° to 1250°C.; this is reduced to 1100° to 1060°C. in successive chambers, 900°C. being reached in the fifth chamber where the last burning of the gas occurs. The temperature of the fifth chamber is the most important. The temperature of the lower chambers should not exceed 650°C. The heat required for an output of 10 tons per day is 20 therms. The cost of 12 retorts complete with foul main and coal elevator is £16,000. This plant would treat 30,000 tons per annum. A set of six retorts erected in 1935 at the South Yorkshire Chemical Works, Parkgate, Rotherham, England, has worked satisfactorily. Six additional retorts have since been erected. For Part I see *Ceram. Abs.*, **12** [7] 275 (1933); **13** [4] 99 (1934); see "Report . . . ," *ibid.*, **17** [3] 114 (1938). A.B.S.

PATENTS

Apparatus for exfoliation of vermiculite. P. S. DENNING (F. E. Schundler & Co., Inc.). U. S. 2,265,358, Dec. 9, 1941 (Oct. 5, 1938).

Bonding refractory materials. O. G. BENNETT AND L. B. BERGER. U. S. 2,265,682, Dec. 9, 1941 (April 18, 1939).—(12) That method of making a bonded metallic chromite product which comprises forming a mixture of chromic oxide, a minor proportion of bentonite and of carbon, and water in an amount to render the mass moldable, molding the mixture, heating the formed mass to a temperature at least high enough to irreversibly dehydrate the bentonite, impregnating the mass with a chromate heating to at least about 300°C., burning carbon from the mass, impregnating the burned mass with the chromite and heating, and thereby producing a strongly bonded, hard, refractory mass.

Firebox arch construction of locomotive-type boilers. AMERICAN ARCH CO. Brit. 540,380, Oct. 29, 1941 (Oct. 14, 1939).

Furnace wall. M. H. KUHNER (Riley Stoker Corp.). U. S. 2,263,004, Nov. 18, 1941 (Feb. 14, 1939).—A water-cooled furnace wall.

Refractories. EDWARD STEPHAN (Rheinische Chamotte- und Dinas-Werke). Ger. 699,233, Oct. 24, 1940; 80*b*. 8.22; *Chem. Abs.*, **35**, 6756 (1941).—To a clay slip are added Al_2O_3, bentonite (both in a fine state of subdivision), and water. While the volume increases greatly, the former consistency is retained. The additions are such that the molar ratio of any of the aluminosilicates is maintained. Electrolytes are added if necessary. The processing of this mixture is as usual. HEINRICH VAN THIEL (I. G. Farbenindustrie A.-G.). Ger. 699,760, Nov. 7, 1940; 80*b*. 8.18; *Chem. Abs.*, **35**, 7138 (1941).—The residue of alkaline decomposition of chrome ore is briquetted and calcined at 1500°. The sintered material is ground and mixed with 5% of the same material but uncalcined. It is properly moistened, formed into blocks, and fired at 1450°.

Refractory blocks and method of producing. R. HADDAN (Corning Glass Works). Brit. 540,484, Oct. 29, 1941 (Dec. 13, 1939).

Refractory lining for furnaces, etc. H. C. RATEAU (American Arch Co.). U. S. 2,264,551, Dec. 2, 1941 (March 16, 1939).

Refractory material, such as high-temperature insulation brick for furnace linings, etc. A. R. LUCAS AND L. R. J. LUCAS. Brit. 540,182, Oct. 22, 1941 (May 4, 1940); addition to 539,957, Oct. 15, 1941 (April 25, 1940).

Terra Cotta

Flagstones, tile, wall tile. M. BIRKENBIHL. *Keram. Rundschau*, **48** [18] 149–51; [20] 167–69 (1940).—Flagstones were first made in Asia Minor to create, besides a decorative effect, a cooling effect in the high temperatures of the climate. Ispahan (in Iran), Damascus, and Cairo were the centers of manufacture. In the 13th century, flagstones and tile were combined to form mosaics, especially in western Asia. This type of ceramics was brought to Europe by the crusaders and perhaps also through trade routes. In Spain, particularly, a high degree of art was reached; large pieces 40 to 43 cm. long and 4 cm. thick weighing 10 kgm. are still in existence, sometimes at a height of 1 m. The art spread all over Europe and is at present again in vogue. The modern German development is described, and many pieces are illustrated. M.H.

Heating elements of porcelain. M. REUTER. *Keram. Rundschau*, **48** [41] 333–34 (1940).—The use of ceramic radiators is discussed, and the conditions under which they can compete economically with cast-iron radiators are explained. Radiation, expansion under low-pressure steam, weight, interchangeability of parts, and life must at least be equivalent to those of cast-iron heaters and eventually superior. A fairly high-grade porcelain is generally suitable for this purpose. Specific examples are described. M.H.

Lightweight interlocking clay shingle. ANON. *Brick & Clay Record*, **99** [5] 21 (1941). B.C.R.

PATENTS

Ceramics and their manufacture. GENERAL ELECTRIC CO., LTD., J. H. PARTRIDGE, AND M. PIRANI. Brit. 540,543, Nov. 5, 1941 (Aug. 14, 1940).

Making ceramic products. D. E. LOWER. U. S. 2,266,646, Dec. 16, 1941 (Dec. 5, 1938).—The method of making glazed ceramic products comprising mixing a soluble phosphate and water with selected clays, the phosphate being in an amount between 0.5 and 3% by weight of the mix, forming from the resultant mixed mass ceramic bodies of the desired shapes, drying the bodies, and subsequently firing them.

Whiteware

Experiments for the liquefaction of clay. E. Bayer. *Keram. Rundschau*, **48** [42] 341–43 (1940).—Experiments made to determine the best casting conditions for clays and clay mixtures and their consistencies are described in detail. The tests were made by determining the time required by the mass diluted with water to flow out of a container under definite conditions, with and without other substances or electrolytes, such as NaOH, Na_2CO_3, Na_2SiO_3, humic acid, and tannic acid. The correct concentration of water and the amount of electrolyte to be added differ for each clay. The best mixture proved to be NaOH and Na_2SiO_3 in the ratio of 4:1, with an addition of humic acid. NaOH, Na_2CO_3, and Na_2SiO_3 behave similarly and liquefy clay even in comparatively small amounts, while humic acid and tannic acid merely widen the liquefaction range. Tables give the minimum amount of the suitable electrolyte for the same water content of three different clays; the lowest water content was found to be 20 to 25% for fat clay; this corresponds to the water content of any finished mass for pots if formed dry. Additions to make the clay lean have practically no effect on liquefaction. When mixing different clays, the arithmetic mean of the additions for the individual clays seems to be the correct addition for the mixture. M.H.

Improvements in pottery working conditions. T. Dymock. *Trans. Brit. Ceram. Soc.*, **40** [7] 295–317 (1941).—D. discusses the manner in which lead poisoning has been practically eliminated as a health hazard in the pottery industry. Silicosis is also being eliminated by the substitution of alumina for flint in china bedding and for siliceous abrasives in polishing. Ventilation, the guarding of machinery, and the general welfare of workers are also discussed. R.A.H.

Modulus of elasticity of dinnerware bodies by a sonic-vibration method. S. V. Forgue and G. A. Loomis. *Bull. Amer. Ceram. Soc.*, **20** [12] 425–30 (1941).—11 references, 5 figures.

Stress-strain characteristics of plastic clay masses. R. Russell, Jr., and C. F. Hanks, Jr. *Jour. Amer. Ceram. Soc.*, **25** [1] 16–28 (1942).—12 references, 20 figures.

Structures of unfired pottery bodies revealed by a new technique. W. O. Williamson. *Trans. Brit. Ceram. Soc.*, **40** [7] 275–94 (1941).—The method devised by A. V. Weatherhead for obtaining pyroxylin "peels" from natural clays for microscopical study has been adapted in a convenient form to the investigation of whiteware bodies. It throws light on the nature of the nonplastics and on any structural parallelism which they may exhibit. Three varieties of structural parallelism are recognized. They result from the following causes: (*a*) *Filtration* (in filter-press cakes and cast pieces), where planar parallelism is involved. (*b*) *Plastic flow* (in pugged clay and jollied and jiggered ware). Both planar and linear parallelism occur in pugged clay and probably in jollied and jiggered ware. In the latter, planar parallelism is certainly present. (*c*) *Flow of dust in filling tile dies.* Filter-press cakes show particles with a general orientation parallel to the surfaces of the cakes. There is a similar arrangement in cast bodies; the presence of parallel structures, therefore, is no proof that a body was made by a plastic process. The parallel structures in pugged clay tend to follow the length of the column and not the breadth, both in straight extruding and right-angled pugs. These structures may give place, in the interior of the column, to semi-ellipsoidal *schalieren* directed away from the die. The results of the structural investigation of pugged clay are in harmony with those obtained by Cloos *et al.* from the study of flow problems where plastic clay was used to represent the igneous material. Jollied and jiggered ware show structural parallelism to the surfaces of the pieces. Dust-pressed tile have no marked parallelism to the tile faces, but it occurs from the flow of dust in die filling. R.A.H.

Study of glaze and body interface. C. W. Parmelee and Paul E. Buckles. *Jour. Amer. Ceram. Soc.*, **25** [1] 11–15 (1942).—13 references, 6 figures.

PATENTS

Article of ceramic or vitreous material. A. O. Austin. U. S. 2,264,428, Dec. 2, 1941 (June 22, 1935; Oct. 26, 1939).

Ceramic article manufacture. R. W. Erdle (Dental Research Corp.). Can. 400,438, Nov. 4, 1941 (Feb. 24, 1939). G.M.H.

Condenser bushing. J. H. Frakes (Westinghouse Electric & Mfg. Co.). U. S. 2,263,768, Nov. 25, 1941 (Feb. 20, 1940).

Forming a metallic surface on ceramic bodies. D. H. Rowland (Locke Insulator Corp.). U. S. 2,264,152, Nov. 25, 1941 (April 27, 1938).

High dielectric constant ceramic material. Louis Navias (Canadian General Electric Co., Ltd.). Can. 400,806 and 400,807, Nov. 18, 1941 (Jan. 17, 1939). G.M.H.

Insulating structure. W. H. Wells and A. M. Wahl (Westinghouse Electric & Mfg. Co.). U. S. 2,264,685, Dec. 2, 1941 (June 28, 1940).

Insulator and method of manufacturing. W. H. Burleson (Ohio Brass Co.). U. S. 2,262,831, Nov. 18, 1941 (March 1, 1940).

Sagger pin. W. W. Irwin (Potters Supply Co.). U. S. 2,263,212, Nov. 18, 1941 (Oct. 16, 1940).

Sealing metals to ceramic bodies. Hans Pulfrich and Richard Magner (Patent-Treuhand-Ges. für elektrische Glühlampen m.b.H.). Ger. 701,508, Dec. 19, 1940; 80*b*. 23.01; *Chem. Abs.*, **35**, 8232 (1941).—The ceramic body contains one or more of the oxides of Th, Hf, Ti, and especially Zr. A suitable ceramic body is made of, e.g., ZrO_2 4, steatite 85, and kaolin 11%. The place where the seal is to be placed on the ceramic body is covered with Mo or Re powder. The powder is burned in, but the particles should not be sintered. For the sealing a hard solder is used, e.g., one made of a Ag-Cu-Ni alloy. The coefficients of expansion of the ceramic body and the metal do not have to be similar. The melting point of the solder should be below the elasticity limit of the ceramic body. When properly made, these seals are vacuum tight; they can also be used in sealing ceramic bodies to other ceramic bodies.

Sparking plugs for internal combustion engines. Lodge Plugs, Ltd., and C. J. Smithells. Brit. 540,537, Nov. 5, 1941 (June 22, 1940).

Spark plug. D. H. Corbin and R. R. Barrington (General Motors Corp.). U. S. 2,265,352, Dec. 9, 1941 (March 31, 1941). H. K. King. U. S. 2,262,769, Nov. 18, 1941 (Feb. 19, 1941).

Spark plug. Tullio Tognola (Bendix Aviation Corp.). Can. 399,606, Sept. 30, 1941 (June 7, 1939; in U. S. June 25, 1938). G.M.H.

Thin ceramic tubes and plates. Rosenthal-Isolatoren G.m.b.H. Werk Selb. Ger. 699,664, Nov. 7, 1940; 80*a*. 46; *Chem. Abs.*, **35**, 7139 (1941).—Filter paper is rolled into a tube and is saturated with the slip. After drying it is fired. The paper is ashed, and the tube is sintered by stepping up the temperature gradually. By this method strong tubes and plates with a thickness of a few hundredths millimeter are obtained.

Vacuum-tight sealing of ceramic to ceramic or ceramic to metallic bodies. Horst Schillbach (Siemens & Halske A.-G.). Ger. 700,840, Nov. 28, 1940; 80*b*. 23.10; *Chem. Abs.*, **35**, 8232 (1941).—The ceramic areas to be joined are covered with a high-melting base-metal layer. A suitable solder is a Cu-Ag alloy containing 28% Cu. Its melting point is 788°.

Equipment and Apparatus

Automatic level controllers. M. F. BEHAR. *Instruments*, **14** [11] 326–80 (1941).—B. presents a survey of devices and systems for automatically controlling the level of liquids and bulk materials. The equipment of 63 manufacturing concerns is described with layouts and drawings. B.C.R.

Drier troubles mean die troubles: II, Core taper, die construction, and lubrication. GEORGE C. SELLS, JR. *Brick & Clay Record*, **99** [2] 26, 28 (1941).—In tile manufacture, incorrect tapering of the core caused excessive cracking of tile at the webs; correcting the taper resulted in a decrease in drier loss from 30 to 2%. In general, the more plastic clays or shales require less core taper than the coarser nonplastic types. Lubrication of the die resulted in increased speed and lower power consumption. **III, Bridge construction for clayware dies.** *Ibid.*, [3] 20–22.—In the manufacture of hollow tile, the location of the bridge determines to what extent a satisfactory bond may be obtained. Final bonding is dependent on the plasticity and particle size of the clay and on the pressure developed within the die. With the H type of bridge, it is advisable to speed up the slow places rather than to slow down the faster ones in attempting to obtain the proper balance of the die. The use of drags over the bridge results in greater power consumption and reduced output of the die. Means of obtaining the proper spacing of bridge openings is described. For Part I see *Ceram. Abs.*, **21** [1] 19 (1942). B.C.R.

Gamma rays used to detect flaws in steel. ANON. *Machinery* [N. Y.], **47** [10] 121 (1941).—Radium sulfate is used to make gamma-ray photographs of steel structures up to 10 in. in thickness; the equipment is briefly described. See *Ceram. Abs.*, **20** [9] 221 (1941). R.H.B.

High-temperature metallic-resistor furnaces. W. KROLL. *Trans. Electrochem. Soc.*, **79**, 199–214 (1941).—In the past, high-temperature metallic-resistor furnaces have generally been small, and, with the exception of the tungsten-lamp factories, their use was limited to laboratory experiments. The new furnaces described are large enough for plant practice. They can be operated continuously. The most suitable type provides for free expansion of the suspended rugged resistor composed of heavy tungsten wires. A protective gas within the furnace, such as dry hydrogen, is an important and essential feature of these tungsten-molybdenum resistor furnaces. A maximum temperature of 2000°C. is attainable. The method for sintering ceramic cores made of highly refractory oxides is briefly described, and the properties of the cores are discussed. Illustrated. F.G.H.

Photoelectric cooling control. P. EWALD. *Electronics*, **14** [11] 55, 80–81 (1941).—Hot phosphate ore on a conveyer passes under an infrared sensitive photoelectric relay which operates a solenoid valve to spray cooling water on the ore as it is needed. The device is used at the TVA Fertilizer Works, Wilson Dam, Ala., but is also applicable for other industrial processes which involve calcination of ore and subsequent cooling. Illustrated. H.T.

SEPARATE PUBLICATION

Active List of Permissible Explosives and Blasting Devices Approved Prior to June 30, 1941. J. E. TIFFANY AND Z. C. GAUGLER. *U. S. Bur. Mines Repts. Investigations*, No. 3583, 23 pp. Free.—The characteristics of 189 permissible explosives and blasting devices are given, and the conditions under which they may be used are outlined. R.A.H.

PATENTS

Apparatus for testing frangibility. H. F. SHINDEL (Willson Products, Inc.). U. S. 2,264,412, Dec. 2, 1941 (Dec. 16, 1938).

Clay-cutting device. JOSEF SCHEIBL (Julianna Orbell). U. S. 2,263,474, Nov. 18, 1941 (Jan. 17, 1938).—A machine for making a plurality of closely spaced transverse cuts in extruded plastic material and forming complemental recesses in adjacent blocks of such material.

Driving mechanisms for potters' jiggers, etc. W. BOULTON, LTD., AND C. FARR. Brit. 540,269, Oct. 22, 1941 (June 11, 1940); addition to Brit. 521,631, June 5, 1940 (Nov. 24, 1938).

Drying ceramic bodies. BERTHOLD WEBER AND HANS JOACHIM REUSCH (Siemens-Schuckertwerke A.-G.). Ger. 695,628, Aug. 1, 1940; 82*a*. 1.01; *Chem. Abs.*, **35**, 5665 (1941).—Up to the shrinkage limit (12 to 13% moisture), the body is dried in a high-frequency a.-c. field (3×10^8 Herz $\simeq \lambda = 100$ m.). The drying is finished in the usual way, i.e., the electric drying is applied during the precarious period to obviate spalling.

Electric furnace. W. G. CLARK (Clarkiron, Inc.) U. S. 2,266,002, Dec. 16, 1941 (June 10, 1940).—An electric melting furnace which comprises a refractory member providing a narrow vertically extending melting chamber effective for rapidly heating a moving stream of material to a melting temperature, a conducting material surrounding the refractory, means for inducing currents in the conducting material for heating the refractory to a temperature sufficiently above the melting point of the material to be melted to effect melting of the charge while passing through the refractory member, a restricted outlet for the melting chamber, and a collecting chamber into which melted material from the refractory passes and may be retained in the molten condition by being subjected to a lower heating temperature.

Electrical resistance element. R. S. DEAN (Chicago Development Co.). U. S. 2,263,571, Nov. 25, 1941 (April 13, 1939). U. S. 2,263,572, Nov. 25, 1941 (Oct. 23, 1939).

Kilns, Furnaces, Fuels, and Combustion

Calorific value of carbon in coal: the Dulong relationship. R. A. MOTT AND C. E. SPOONER. *Fuel*, **19**, 226–31, 242–51 (1940); *Jour. Soc. Glass Tech.*, **25** [109] 170A (1941).—From an analysis of the U. S. Bureau of Mines' data for the calorific values of cokes prepared from 28 coals of varying rank at different temperatures it was concluded that the calorific value of C in bituminous coal could be taken as 8000 ± 10 cal. per gm. Using this value, increased to 8030 to allow for the heat of decomposition of the coal, with Rossini's value for the calorific value of hydrogen at constant volume (33,900 cal. per gm.), and assuming that two-thirds of the oxygen was combined with hydrogen, the remainder being associated with CO and CO_2 groups, a modified Dulong formula for Q, the calorific value of coal, was derived: $Q = 80.30C + 339H - 34.70$ on the Parr basis, or $Q = 80.30C + 339H - 34.70 + 22.5S$ on the dry, ash-free basis. A tentative value of 7900 cal. per gm. was suggested for the calorific value of C in oven cokes.

Colloidal fuel. J. E. HEDRICK. *Mech. Eng.*, **63** [8] 591–94 (1941).—Technical problems involved in the economic use of oil-coal fuels are discussed. Illustrated. F.G.H.

Flue-gas analysis made easy. CHAS. HUBBARD. *Power Plant Eng.*, **45** [10] 106, 108 (1941).—Easily constructed charts facilitate calculations of flue-gas analyses from Orsat readings for a given oil or gas whose carbon and hydrogen content are known or can be approximated. Illustrated. B.C.R.

Formula for calculating the heating value of coals from the elementary analysis. L. SÜMEGI. *Gas- & Wasserfach*, **83** [30] 357–59 (1940).—A new formula is developed which gives better agreement with the calorimetric determination than the formulas of Steuer, Lant, Dulong, or Schuster. The formula for the upper heating value is $H_U = [81C + O/2\ (0.75)] + 345[H - O/2\ (0.125)] + 25S$, and that for the lower heating value is $H_L = 81[C + O/2\ (0.75)] + 285[H - O/2\ (0.125)] + 25S - 6w$. The calculation

from the analysis of 14 different coals (German, Bulgarian, Russian, Turkish, Czechoslovakian, and Hungarian) with heating values from 4365 to 8106 gave close agreement with the calorimetric determination; determination by the other formulas showed differences up to 2½ to 3%. M.H.

Silicon carbide electrode. D. N. Hume and I. M. Kolthoff. *Jour. Amer. Chem. Soc.*, **63** [10] 2805–2806 (1941).—Silicon carbide acts as an oxidation-reduction electrode, like platinum or other noble metals. The results of earlier workers, which differ from those of the authors, are attributed to a direct contact between solution and metallic conductor and not to any property of the silicon carbide. Illustrated. F.G.H.

Turbulence and combustion in the pulverized-coal furnace. B. J. Cross. *Mech. Eng.*, **63** [3] 203–207, 210 (1941).—The various methods of firing pulverized-coal furnaces are described, together with burner types and arrangements. The importance of turbulence in obtaining complete combustion is discussed in detail. Illustrated. F.G.H.

Geology

Chemical properties of andalusite. J. Jakob. *Schweiz. Mineralog. & Petrog. Mitt.*, **20**, 8–10 (1940); *Chem. Abs.*, **35**, 5418 (1941).—Precious andalusite (I) from Minas Geraes, Brazil, and common andalusite (II) from Fop-Tiamarsch, Graubunden, were analyzed. I contained 0.23 MgO, 0.40 Na_2O, and 0.21% K_2O, while II contained no MgO, 1.63 Na_2O, and 2.36% K_2O. The pure alkali-poor I is very rare compared with II, which is interspersed with a micaceous mineral. It is believed that the lattice of andalusite is stabilized by the presence of alkali atoms and that the micaceous mineral is a later product of separation. I is rare because it can originate only under special conditions, while in the case of the alkali-rich II the micaceous mineral always separates out.

Chemistry of clay. U. Hofmann. Presented before Ver. Deut. Chem., May, 1940. Abstracted in *Angew. Chem.*, **53** [51–52] 595 (1940).—H. reviews work on the swelling of bentonites and the role of interplanar water. The relative effects of alkali and alkaline-earth ions are also considered. R.L.G.

Densities of molten rocks and minerals. E. B. Dane, Jr. *Amer. Jour. Sci.*, **239** [11] 809–18 (1941).—Density and thermal expansion were determined for liquid synthetic diopside and akermanite and for natural bytaconite and diabase by measuring the loss in weight of a platinum ball when submerged in the fused minerals. The results for diabase are compared with those found by other investigators. Rough values of the surface tensions are included. The apparatus and procedure are described in detail. B.C.R.

Determination of exchange constants for the soil cations. T. F. Antipova-Karataeva and I. N. Antipov-Karataev. *Pochvovedenie*, **1940**, No. 2, pp. 52–65; *Chem. Abs.*, **35**, 6037 (1941).—The quantitative laws governing adsorption of cations by soils are still to be established. This is especially true of mixtures of two or more salts. A theoretical interpretation of the experimental material published earlier is given. In these experiments the exchange reactions between two and three cations in black soil were investigated. The condition of constancy of the ionic force of the solutions (J) was strictly adhered to in all experiments of a given series. The value of J = constant was always calculated from the Lewis equation. Under these conditions the exchange-adsorption reactions were shown to obey the law of mass action. They were also found to be reversible. For pairs of cations it was found that $X_1/X_2 = C_1K/C_2$, where C_1 and C_2 are the concentrations of cations in equivalent solutions, and X_1 and X_2 are the concentrations of the adsorbed cations for the case where both of them are of the same valence. When valences are different, $X_1/\sqrt{X_2} = C_1K/\sqrt{C_2}$ for the case where one is univalent and the other is bivalent. When three ions are present, the value of K between them taken in pairs will be the same within 10 to 15% as if the third cation were absent. The exchange constant, K, is thus practically independent of the nature of ions other than the given pair and of the value J of the solutions. The average values found are, for black soil, $K_{MgCa} = 0.3830$, $K_{NaCa} = 0.0686$, and $K_{NaMg} = 0.111$. Each of these can be calculated from the other two: $K_{NaCa} = K_{NaMg}\cdot\sqrt{K_{MgCa}}$. The experimental method is new and applies to both soils and clays. It permits preliminary quantitative investigation of soil properties in respect to adsorption for the purpose of amelioration measures, especially in saline and solonetz soils. The K values can be determined from 3 or 4 "points" if J is constant. If three cations are present, only two K values need be experimental. The exchange of any other cation can be studied in the presence of a known pair, if the concentration of the former in the given soil is known. With the aid of the above experiments it was possible to establish the exact ratios of Na : Ca and of Na : (Ca + Mg) in the soil solutions at which the Na ions begin to penetrate into the colloidal complex of the soil (the potential saltiness of soil). Such quantitative experiments are relatively more simple than the difficult empirical procedures used in the present-day practice of saline soil amelioration. The next problem is to establish accurately the amplitude of fluctuations in the above K values for various cations in different soils. It will then be possible to calculate beforehand, on the basis of the composition of soil solutions and of the chemical nature and concentration of each cation present in the soil, the best measures to be followed in practical and theoretical problems. 31 references.

Electrochemical deposition of soils by the method of L. Casagrande. E. Kumutat. *Angew. Chem.*, **53** [15–16] 168–71 (1940).—The application of aluminum electrodes to the process of electrodeposition of soils is considered from the viewpoint of colloidal chemistry. At the anode, the exchangeable cations (e.g., Na^+) are secured as aluminates, while from both electrodes an active $Al(OH)_3$ is formed which stabilizes the coagulation process. R.L.G.

Geological investigation of the chromite deposits of California. J. E. Allen. *Calif. State Min. Rept.*, No. 37, pp. 101–67 (1941); abstracted in *Econ. Geol.*, **36** [6] 666 (1941).—About 234 chrome deposits are described and classified according to the following major structural features: (1) number, (2) size, (3) shape, (4) attitude of major axes, (5) degree of serpentinization, and (6) structures within the ore body. With one exception, none of the chromite deposits studied could be placed in the category of magmatic segregations in place. Although differentiation of chromite may begin before intrusion, it is more probable that it takes place during and even after intrusion. 31 illustrations. B.C.R.

Hydrothermal syntheses of silicates. Review of the chemistry of clay minerals. W. Noll. Presented before Ver. Deut. Chem., Leipzig, March, 1940. Abstracted in *Angew. Chem.*, **53** [21–22] 240 (1940).—The investigations of the hydrothermal syntheses of $Al_2O_3\cdot SiO_2\cdot H_2O$ and $MgO\cdot SiO_2\cdot H_2O$ minerals are reviewed. R.L.G.

Importance of the nature of the valence bond for the desorption of cations. N. I. Gorbunov. *Pochvovedenie*, **1940**, No. 3, pp. 54–66; *Chem. Abs.*, **35**, 6038 (1941).—In the soil the different mineral elements are retained through the action of physicochemical forces, among which the valence bonds of three different types (covalent, polar, and ionic) are the most important. Very often two or three types of bond operate together, as in the case of the adsorbed H, which is usually found in the soil as a constituent of organic acids. Here both ionic and covalent valences hold H atoms in the molecule. On the basis of the valence theory applied to electrolytes and colloids, and as a result of experiments reported previously and also briefly in this paper, it is concluded that electrovalence acts chiefly in the adsorption of metallic cations usually present in the form of crystals. This bond is very strong, but in some crystals, such as

mica, there are some directions along which desorption can take place; the cleavage plane between the mica layers is the plane where exchange of cations and removal of K ions takes place, causing considerable erosion. In orthoclase, the lattice is held together both by the ionic and covalent forces, the K ions being inside of the lattice. The K ion, therefore, cannot be so easily removed from this lattice, and orthoclase is resistant to erosion. As H is held in the organic acids by weak ionic and strong covalent forces, the desorption of hydrogen from soil is not as pronounced as that of the metallic cations. The present experiments show that NH_4Cl can easily displace Mg and Ca ions but does not easily displace H ion. Desorption of metallic cations from soil is less if the soil contains adsorbed H. This was proved by treating soil with NH_4OAc solution; the soil forms acetic acid, and thus H is removed from the soil while the metal cations are still held by the soil surface. Salts of weak acids retard, while salts of strong acids promote, desorption. This explains the genesis of podzol soils to some extent and indicates the importance of introducing $CaCO_3$ to prevent desorption of needed cations. 34 references.

Infrared as an analytical tool: dehydration of silicic acid derived from feldspars. E. W. KOENIG. *Bull. Amer. Ceram. Soc.*, **20** [12] 447–50 (1941).—9 references.

Ionic effects on the rate of settling of fine-grained sediments. L. R. DREVESKRACHT AND G. A. THIEL. *Amer. Jour. Sci.*, **239** [10] 689–700 (1941).—The effect of Na^+, K^+, and Mg^{++} ions in strengths of 0.01 to 1.0 molar solutions on the settling rate of such sediments as marl, shale, silt, kaolinite, illite clay, plastic fire clay, varved glaciolacustrine clay, volcanic ash, bentonite, and diatomaceous earth is discussed. Mg ions were considerably more effective as a coagulator than either K or Na ions, there being little difference between the latter two. The more rapid settling rates of flocculated clays produced thicker sediment layers. The larger flocculates formed by the divalent ions do not pack as closely as the smaller aggregates formed by the univalent ions. Chemical or mineralogical variations in fine sediments have little influence on the rate of sedimentation. B.C.R.

Measurement and geological significance of shape and roundness of sedimentary particles. W. C. KRUMBEIN. *Jour. Sed. Petrology*, **11** [2] 64–72 (1941).—A method for the rapid measurement of the shape and roundness of large particles is described. Shape is determined from the long, intermediate, and short diameters. Roundness is measured by a rapid visual method. Shape and roundness are influenced differently during abrasion and selective transport and are therefore important in evaluating the effect of these processes during the formation of the deposit. G.M.H.

Minerals in dolomite of Campolungo (Tessin). E. GUBELIN. *Schweiz. Mineralog. & Petrog. Mitt.*, **19**, 325–442 (1939); abstracted in *Chem. Zentr.*, **1940, II**, 2138.—After reviewing the geological structure of the Campolungo and Cadonighino Passes, G. describes the minerals occurring in the dolomite. Apatite, calcite, chrysoberyl, dolomite, fahlerz, fluorite, fuchsite, graphite, muscovite, talc, and titanite are mentioned briefly. The diaspore is very pure; it is discussed from the crystallographic standpoint. Disthene forms blue to sky-blue crystals of the following percentage composition: 37.21 SiO_2, 60.80 Al_2O_3, 0.33 Fe_2O_3, 0.78 Na_2O, 0.32 K_2O, 0.83 H_2O^+, and 0.08 H_2O^-. Their specific gravity is 3.527. Grammatite occurs in white, green, gray-black, and brown crystals and exhibits the most varied habits. The optical study of the white variety showed a refraction of light of $n_\alpha = 1.6042$, $n_\beta = 1.6082$, and $n_\gamma = 1.6199$. For the green variety, $n_\alpha = 1.6052$, $n_\beta = 1.6093$, and $n_\gamma = 1.6211$; for the gray-black type $n_\alpha = 1.6094$, $n_\beta = 1.6132$, and $n_\gamma = 1.6253$. The white contains 0.47% FeO but no Fe_2O_3, and the green contains about 0.6% Fe_2O_3 and 0.5 to 0.9% FeO; the gray-black has about 1.0% Fe_2O_3 and 8.0% FeO. Corundum occurs in a red and blue variety and forms crystallographically well-defined crystals. The spectroscopic determination corresponded with that of specimens of rubies (Cr and Fe) and sapphires (Ti and Fe) of other deposits. Orthoclase is rare. Phlogopite is a characteristic mixture and forms blond to brown crystals with all shades between. It is thinly foliated and has the following composition: 40.45 SiO_2, 0.83 TiO_2, 16.42 Al_2O_3, 1.31 Fe_2O_3, no FeO, 0.02 MnO, 25.81 MgO, no CaO, 1.02 Na_2O, 8.25 K_2O, 5.79% H_2O^+, and no H_2O^- or F. Pyrite is abundant; its forms are described. Quartz is treated crystallographically. Rutile is rare, and its forms and physical properties are varied. Scapalite has a refraction of light of $\epsilon = 1.5580$ and $\omega = 1.5865$ and contains 71 parts mejonite and 29 parts marialith. Green and brown tourmaline are described fully. M.V.C.

Mullitization of clay in the most important deposits of the U.S.S.R. V. V. GONCHAROV. *Zapiski Vserossiiskogo Mineral. Obshchestva*, **68** [1] 5–17 (1939); abstracted in *Chem. Zentr.*, **1940, II**, 1631.—The loss on firing of different Russian clays (from Chasov-yar, Latnaya Dubrovotschka, and Lubytinsk) at temperatures of 1000° to 1600° showed that the changes in the phase composition of the clay, independent of the chemical-mineralogical composition, are qualitatively constant and that mullite is formed chiefly in the crystalline phase. Up to 1100°, the mullite in the clays is in the form of fine crystals which form an inhomogeneous aggregate. Raising the firing temperature produces a differentiation in addition to the crystal growth. The mullite which separates out of the fired clay contains Fe_2O_3 and TiO_2, whose quantity decreases markedly at higher temperatures. Quantitatively, the mullitization of the clays varies greatly, especially up to 1300°. From 1300° to 1500° the mullitization is the same for all clays except the Chasov-yar clays. The relatively low mullite content of the latter is explained by its chemical-mineralogical composition. Conclusions are drawn on the use of the results concerning mullite content in the manufacture of grog and other ceramic objects. See "Behavior . . . ," *Ceram. Abs.*, **18** [3] 75 (1939). M.V.C.

New Canadian magnesite plant. ANON. *Refrac. Jour.*, **17** [9] 327 (1941).—Brucite and dolomite from the Gatineau Valley will be utilized in a plant producing magnesia and hydrated lime, soon to be constructed. Brick made from magnesia obtained in this manner have given excellent service in copper reverberatory furnaces. B.C.R.

New ideas in synthetic mineralogy. D. P. GRIGOR'EV. *Priroda*, **29** [1] 47–50 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 3009.—As an aid in compensating the time factor in synthetic mineralogy, the use of mineralizers, such as F or compounds of WO_3, or the carrying out of the process of crystal growth at high temperature is considered. The suitability of tests with F instead of with the OH group is referred to. M.V.C.

Orientation of occlusions in calcite and quartz crystals. H. BUTTGENBACH. *Ann. Soc. geol. Belg., Bull.*, **63**, 202–205 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 3009.—Inclusions of pyrite were observed to be oriented along the surface of the scalenohedron d^2 in pieces of clear calcite of Seilles in Belgium. Sagenite was found embedded in three quartz crystals from St. Gotthard; the plane of the inclusion was $10\bar{1}1$ in one case and $11\bar{2}2$ in another. Small rutile crystals were distributed irregularly in the quartz. Although it can be assumed that scalenohedron surfaces in the calcite were formerly covered with pyrite and then underwent further growth, such an explanation for the quartz is not possible. It is not a question of cracks which were later filled with rutile. M.V.C.

Origin and mining of bauxite in Netherlands-India. R. W. VAN BEMMELEN. *Econ. Geol.*, **36** [6] 630–40 (1941).—Bauxite production on Bintan Island (near Singapore) began in 1935 and now amounts to 5 to 6% of the world production. This island is becoming the most important bauxite producer of the Far East. The bauxite is of the aluminous laterite type, having a parent rock that is an aphanitic hornfels with nuclei of feldspar and quartz and a silica content of 65%. The process of laterization was studied in a section exposed by a shaft sunk below the bauxite layer and reaching the unweathered rock at a depth of 52 m. In 1936 the washed ore analyzed Al_2O_3 53,

TiO_2 1.2, Fe_2O_3 13.5, and SiO_2 2.5%. The ore shipped at the present time has a somewhat higher silica content. B.C.R.

Philippine ceramic materials. G. O. OPIANA AND H. MORENO. *Philippine Jour. Sci.*, **74** [4] 385–87 (1941).—Ceramic products imported into the Philippines in 1938 amounted to two million dollars. Brick and tile clays are found in many places. While there is no kaolin mining in the Philippines, there is a white-firing clay that analyzes 55.99 SiO_2, 28.77 Al_2O_3, 0.89 Fe_2O_3, 0.89 CaO, 0.03 MgO, 0.08 Na_2O, and 0.09 K_2O; ignition loss 11.59%. B.C.R.

Physicochemical effects of treating some of the Indian bentonites with sodium carbonate. R. C. HOON AND GANGA SINGH AHLUWALIA. *Jour. Indian Chem. Soc., Ind. & News Ed.*, **4**, 29–34 (1941); *Chem. Abs.*, **35**, 6752 (1941).—If Kashmir and Jodhpur bentonites are treated with 5.3 and 1.3% Na_2CO_3, respectively, their swelling properties increase. When 3 or 4% of the treated Kashmir bentonite is mixed with sand, the rate of percolation is reduced to 0.12 or 0.06 cc. of water per min., respectively; Kashmir bentonite can therefore be substituted for Wyoming bentonite.

Plasticity and pourability of clays. A. SPANGENBERG. *Keram. Rundschau*, **48** [20] 165–67; [21] 175–76; [24] 198–99; [25] 208–209; [27] 223–24 (1940).—S. made exhaustive experiments to find a possible relation between the plastic properties of a clay and its pourability. The latter could not be measured directly, as no instrument gave results which were not influenced by other properties of the clay. The determination was therefore made by letting a liquid with different dilutions (NaOH) flow from a burette onto a definite amount of clay (25 gm.) and mixing both until the mass had a consistency considered satisfactory for practical pouring. Three greatly different clays and two kaolins were used in the tests of the compositions:

	Clays			Kaolins	
	Lôthain	Lautersheim	Anna Mine	Zettlitz	Ebernhahn
Al_2O_3	28.97	38.48	13.37	37.68	27.22
SiO_2	54.89	43.74	79.87	46.62	59.26
MgO	Trace	0.19	0.14		0.29
CaO	0.14	Trace	Trace	0.37	Trace
Fe_2O_3	1.18	1.76	0.95	0.9	1.61
Na_2O } K_2O }	1.59	2.97	2.01	1.10	2.75
Loss on ignition	13.55	12.99	3.48	13.35	8.70

The clay became pourable when mixed with the amounts (in cubic centimeters) of the liquids shown in the following table:

Liquid	Lôthain	Lautersheim	Anna Mine*	Zettlitz	Ebernhahn
2*N* NaOH	40.0	57.5	30	60	65
1*N* NaOH	29.0	77.5	30	65	55
0.5*N* NaOH	16.3	77.5	30	67	70
0.2*N* NaOH	12.5	113.5	30	70	110
0.1*N* NaOH	13.5	112.0	30	70	115
0.05*N* NaOH	14.7	100.0	19	70	115
0.0375*N* NaOH			15.5		
0.025*N* NaOH			16.0	45	73
0.01*N* NaOH	21.5	48	19.0	40	50
0.005*N* NaOH		43		50	50
H_2O	31	61	26.5	50	50

* Approximate.

The tests are described in detail, and the results are summarized as follows: A pourable mass can be considered as a suspension carried by a colloidal clay solution. The clays are related to the colloids as closely as other substances of such fine distribution and of such capacity to adsorb colloid substances. The liquefying action which the alkali exerts on certain clays is due to the formation of a protective colloid for the finest clay particles. The variable action of the alkali with concentration is due to the formation or destruction of the protective colloid. The action of salts and acids on clays containing a protective colloid depends primarily on their behavior with respect to the protective colloid. The plasticity and pourability of clays can be increased artificially by the addition of a protective colloid. 19 references. M.H.

Queries on classification and nomenclature of igneous rocks: II. F. YU. LEVINSON-LESSING. *Compt. Rend. Acad. Sci. U.R.S.S.*, **21**, 129–33 (1938).—Andesites should be considered as a peculiar effusive type, as they are derived from basic magma and have no analogue among intrusive rocks. Rocks of this type may be termed apomagmatic effusions to distinguish them from orthomagmatic effusions. Syenites are to be regarded as apomagmatic intrusions. The genesis of spilites is also dealt with. P.B. & E.S.

Relation of organic matter to color of sedimentary rocks. H. WHITMAN PATNODE. *Bull. Amer. Assn. Petroleum Geologists*, **25** [10] 1921–33 (1941).—Sedimentary rocks may be classified as to color by their reflectivity. Light-colored sediments have a low organic content, and dark-colored sediments a high organic content. Measurements were made on about 3000 samples, the reduction number and the N content being used as measures of the organic content. The relationships of reflectivity to reduction number and of reflectivity to N content vary with respect to the ratio of the N content to the reduction number. The reflectivity of sediments is affected not only by the amount of organic matter present but also by the texture and the content of mineral pigments. G.M.H.

What is kaolin? MENG-CHANG LING. *Science* [China], **25** [5–6] 304 (1941).—The etymology of the word "kaolin" and its origin and kaolinization, types, physical and chemical constitutions, plasticity, drying shrinkage, and heat reactions at various temperatures are discussed. M.C.L.

PATENTS

Concentrating fluorspar ores. C. O. ANDERSON, R. J. STENGL, AND J. G. TREWARTHA (Mahoning Mining Co.). U. S. 2,263,552, Nov. 25, 1941 (Feb. 21, 1940).—In concentrating the fluorspar values of fluorspar ore containing substantial amounts of calcareous material, the steps of finely dividing the ore in soft water having a pH value in excess of 6.5 to thereby form a slime-containing pulp, then frothing the pulp in the presence of a higher fatty acid fluorspar collector and a calcite depressing agent, and returning some of the middlings back of the flotation circuit.

Fluorspar recovery. N. L. SHEPARD. (Aluminum Co. of America). Can. 399,598, Sept. 30, 1941 (April 20, 1939). G.M.H.

Production of magnesium compounds from dolomite. H. H. CHESNY. Brit. 540,139, Oct. 22, 1941 (April 18, 1939).

Chemistry and Physics

Amperometric titrations. I. M. KOLTHOFF. *Trans. Electrochem. Soc.*, **78**, 191–206 (1940).—In amperometric titrations, the current passing through the titration cell is measured. These titrations require little time and are applicable to very dilute solutions. Characteristic current-voltage curves are shown. It is expected that amperometric titrations will find at least as extensive application as that of potentiometric titrations in electroanalysis. F.G.H.

Crystal structures of the tetragonal monoxides of lead, tin, palladium, and platinum. WALTER J. MOORE, JR., AND LINUS PAULING. *Jour. Amer. Chem. Soc.*, **63** [5] 1392–94 (1941). F.G.H.

Determination of metals by means of 8-hydroxyquinoline. R. C. CHIRNSIDE, CELIA F. PRITCHARD, AND H. P. ROOKSBY. *Analyst*, **66** [787] 399–407 (1941).—In the gravimetric determination of certain metals with 8-hydroxyquinoline, accurate results may depend upon the correct

drying temperature. The X-ray diffraction method indicated that anhydrous forms of iron and aluminum complexes may be obtained at 98°C., the zinc complex at 110°C., and the magnesium complex at 160°C. The mechanism of coprecipitation of Zn-Mg and Fe-Al was also investigated by X rays and found to consist of a formation of solid solutions. In each case the separation of the two elements is possible over only a very narrow range of pH. B.C.R.

Electrochemical methods in microchemistry. E. B. ASHCRAFT. *Trans. Electrochem. Soc.*, **78**, 63–76 (1940).—A. presents a review of the detection of the presence of Ag, Cu, Zn, As, and other metals and of the electrolytic quantitative determination of Cu, Hg, Ag, Ni, Sn, Zn, etc., as well as a dozen different acids. Copper determinations have been made on samples weighing as little as 6 μgm., the copper weighing approximately 1 μgm., with a precision of more than 5%. Copper present in an electrolyte to the extent of only 0.5 p.p.m. has been quantitatively determined. Potentiometric titrations have been successfully carried out on electrolyte volumes as small as 0.25 ml. and with dilutions as low as 0.0001 *N* with an accuracy of a few per cent. Arsenic (as little as 0.04 μgm.) can be detected conductometrically. Numerous electro-micro-chemical methods are discussed. F.G.H.

Modified calorimeter for high temperatures. Heat content of silica, wollastonite, and thorium dioxide above 25°C. J. C. SOUTHARD. *Jour. Amer. Chem. Soc.*, **63** [11] 3142–46 (1941).—A calorimeter for high-temperature specific heats (up to 1500°C.) has been constructed which is more easily manipulated and gives results that agree with those of the best previous work. This apparatus is a modification of the standard apparatus, in which a capsule containing the sample is heated in a furnace to a determined temperature and at a given moment dropped into a calorimeter of known heat capacity. The modifications were introduced primarily to remove the necessity for dismantling a considerable portion of the apparatus to return the sample to the furnace in preparation for another determination. This permits more rapid operation than has previously been consistent with good work. The heat content above room temperature has been determined for wollastonite (to 1150°), thorium dioxide (to 1514°), and silica glass (to 1250°C.). The data include simple equations, and the heat capacity is derived therefrom. Illustrated. F.G.H.

Reactions in the solid state between calcium oxide and dehydrated kaolin, mica, feldspar, sillimanite, or mullite. J. ARVID HEDVALL. *Tek. Tid.* [Uppl. A–C, Kemi], **71** [2] 1; [6] 15; [10] 24 (1941).—H. examined the reactivity between 400° and 1100°C. of a number of kaolin minerals, pure or containing feldspar and mica, of sillimanite, and of mullite when mixed with CaO in the solid state. In the case of preparations free from water, preheating at high temperatures or for prolonged periods generally decreases the reactivity at low reaction temperatures (below 800° to 900°C.). The influence is not so marked at higher reaction temperatures, where the reactions are more complex and where the lattice particles possess an increased mobility. In these reactions, as in industrial processes, the different kaolin minerals show a very dissimilar behavior. This cannot be explained as being affected by the mineral impurities. It is evident that the formation of metakaolin, its decomposition, the subsequent transitions of Al_2O_3 and SiO_2, and their recombination are all processes which are profoundly influenced by the methods of preparation, especially the thermal treatment. All kaolin preparations, even if rather impure, will, after preheating at 1000°C. for short periods (about 1 hr. or less), show a maximum of CaO consumption at reaction temperatures of about 500°C. This must be due to the imperfect lattices of the free oxides Al_2O_3 and SiO_2. These are thus highly reactive, and basic compounds are easily formed, especially those of the intermediate type. This shows that topochemical factors may influence the reactions not only quantitatively but also qualitatively. This interpretation is supported by results obtained on heating CaO with sillimanite or mullite. A maximum on the yield curves is obtained by using sillimanite preparations preheated at temperatures where the sillimanite decomposes to give an unstable transition phase. It is not obtained, however, with the stable mullite phase. B.H.S.

Reduction equilibria of zinc oxide and carbon monoxide. E. C. TRUESDALE AND R. K. WARING. *Jour. Amer. Chem. Soc.*, **63** [6] 1610–21 (1941).—Illustrated. F.G.H.

Reflection-transmission relationships in sheet materials. HERBERT F. LAUNER. *Jour. Research Nat. Bur. Standards*, **27** [5] 429–42 (1941); RP 1430. Price 5¢.—Reflectances of transmissive sheets, calculated from the transmissions of one and two sheets, are compared with reflectances obtained by using the General Electric recording spectrophotometer. The expression used as a basis for calculation, $R_a = \sqrt{1-(T_1^2/T_{2a})}$, in which R_a is the reflectance and T_a and T_{2a} are the transmissions of one and two sheets, respectively, of a, was derived by considering the infinite series of reflections undergone by light (or radiant energy in general) in passing through the two sheets. The expression was found to be valid and useful over a wide range of reflectances and wave lengths, for materials such as paper, glass, and an organic plastic. The method is absolute, since it involves no reflectance standard. It involves no spherical or similar integrating device, nor does it involve any reflecting surface other than that of the sample itself as a fundamental part of the measurements. When transmission values for diffuse incidence are substituted into the expression, the reflectances thus calculated correspond to the conditions of diffuse incidence and diffuse viewing and, as such, are somewhat higher than the usual directly measured reflectances for normal incidence and diffuse viewing. For clear sheets with normal incidence, specular reflectance may be calculated. The method thus affords a means of determining, from two simple measurements, the specular-plus-diffuse reflectance of transmissive sheets for diffused light or radiant energy in general. R.A.H.

Specific heats at low temperatures of crystalline boric oxide, boron carbide, and silicon carbide. K. K. KELLEY. *Jour. Amer. Chem. Soc.*, **63** [4] 1137–39 (1941).—Specific-heat measurements of crystalline boric oxide, boron carbide, and silicon carbide were made, covering the temperature range 51° to 290°K. The entropies at 298.16°K. are 13.0 ± 0.1 for boric oxide, 6.47 ± 0.07 for boron carbide, and 3.95 ± 0.04 for silicon carbide. The value $S_{298.16} = 1.7 \pm 0.2$ is suggested for crystalline boron. Illustrated. F.G.H.

Specific heats at low temperatures of ferrous silicate, manganous silicate, and zirconium silicate. K. K. KELLEY. *Jour. Amer. Chem. Soc.*, **63** [10] 2750–52 (1941).—Specific heat measurements of Fe_2SiO_4, $MnSiO_3$, and $ZrSiO_4$ were made in the temperature range 51° to 298°K. Fe_2SiO_4 has a marked maximum in its specific-heat curve, with the peak at 65.0°K. The entropies at 298.16°K. are 35.4 ± 1.4 for Fe_2SiO_4, 21.3 ± 0.3 for $MnSiO_3$, and 20.1 ± 0.3 for $ZrSiO_4$. The free energies of formation from the elements have been computed for $MnSiO_3$ and Fe_2SiO_4 as $\Delta F^\circ_{298.16} = -282{,}100$ and $\Delta F^\circ_{298.16} = -324{,}800$, respectively. Illustrated. F.G.H.

Synthetic production of amphibole from pyroxene melts. D. P. GRIGOR'EV AND V. V. GURETSKAYA. *Zapiski Vserossiiskogo Mineral. Obshchestva*, **68** [2] 556–58 (1939); abstracted in *Chem. Zentr.*, **1940, II**, 3456.—No change occurs in pyroxene melts in the absence of volatile components; pyroxene was obtained, however, in amphibole melts under the same conditions. The pyroxene formation did not occur if F was added as a volatile component. Conversely, pyroxene changes to amphibole when fused in the presence of NH_4F. The experiments showed that the presence or absence of volatile substances appears to be an essential factor in the formation of pyroxene or amphibole in magma. M.V.C.

Ternary system pseudowollastonite–akermanite and gehlerite. E. F. OSBORNE AND J. F. SCHAIRER. *Amer. Jour. Sci.*, **239** [10] 715–63 (1941).—In this ternary system only two crystalline phases in equilibrium with liquid are possible, viz., an akermanite-gehlerite solid solution (mel-

ilite) and α-$CaSiO_3$ (pyroxenoid). There is no ternary eutectic, and the lowest temperature at which liquid is present is 1302°C. at the ternary minimum on the boundary curve between the fields of melilite and α-$CaSiO_3$. The composition at the ternary minimum is $CaSiO_3$ 51, $Ca_2MgSi_2O_7$ 20, and $Ca_2Al_2SiO_7$ 29%. B.C.R.

Thermal, microscopic, and X-ray study of the system $NaPO_3$–$Na_4P_2O_7$. EVERETT P. PARTRIDGE, VICTOR HICKS, AND G. W. SMITH. *Jour. Amer. Chem. Soc.*, **63** [2] 454–66 (1941).—From the combined evidence obtained by thermal studies, high-temperature microscopy, and X-ray investigation of the system $NaPO_3$–$Na_4P_2O_7$, the following conclusions are drawn: (1) Sodium metaphosphate may be obtained by thermal processes in three crystal forms. (2) Tetrasodium pyrophosphate probably exists in five crystal forms, but, since all transformations are reversible, only one form can be obtained at ordinary temperatures. (3) Only one of the hypothetical polyphosphates in the system $NaPO_3$–$Na_4P_2O_7$ actually exists as a crystalline individual. This is sodium tripolyphosphate, $Na_5P_3O_{10}$, which can be obtained at ordinary temperatures in either of two crystal forms. Illustrated. F.G.H.

Thermal properties of crystalline and glassy boron trioxide. J. C. SOUTHARD. *Jour. Amer. Chem. Soc.*, **63** [11] 3147–50 (1941).—The heat content above 298°K. has been determined for crystalline B_2O_3 to near the melting point and for glassy B_2O_3 to 1777°K. The heat of the reaction B_2O_3 (crystals) → B_2O_3 (glass) has been determined at 298.1°K. as 4360 ± 20 cal./g.f.w. The free energy of the reaction B_2O_3 (crystals) → B_2O_3 (glass) is calculated to be 2600 cal./g.f.w. at 298.1°K. The entropy of B_2O_3 glass is calculated to be 18.9 ± 0.3 at 298.1°K. An equation has been derived for the free energy of formation of liquid B_2O_3 at temperatures above 1000°K. Illustrated. F.G.H.

Thermodynamic properties of the crystalline forms of silica. MAX A. MOSESMAN AND KENNETH S. PITZER. *Jour. Amer. Chem. Soc.*, **63** [9] 2348–56 (1941).—An extensive analysis is given of the thermodynamic properties of the various crystalline forms of silica. The new experimental data presented are the heat content above 25°C. of quartz, tridymite, and cristobalite. For each of the latter modifications, about thirty experimental values are given in the range 90° to 350°C. In the range 400° to 550°C. the difference between the heat content of tridymite and cristobalite was measured. These results were combined with data from the literature to yield values of the following quantities for quartz, tridymite, and cristobalite: the heat content function $(H_T^\circ - H_0^\circ)$, the free energy function $(H_0^\circ - F_T^\circ)/T$, the entropy, and the heat capacity for each form over the range 298° to 2000°K. The differences in heat content of the three forms are given for 0° and 298°K. All heat-of-fusion data are reduced to a comparable basis, and a best value is selected. The temperatures, heat, entropy, volume changes, and pressure-temperature coefficients are given for the various transitions between the principal modifications and for transitions within one principal modification. The standard free energy differences between the modifications are calculated and plotted, chiefly to show the stability relationships between the various forms. Among the results obtained are (1) the minimum pressure under which liquid silica freezes directly to quartz and (2) the metastable melting points of quartz and tridymite at 1 atm. pressure. It was found that cristobalite is more stable than tridymite, not only above 1743°K. but also below 450°K. The low-temperature transitions of cristobalite and tridymite are discussed in terms of the beginning of a revolution of oxygen atoms in small circular orbits. Illustrated. F.G.H.

Water glass. BRUNO SCHWEIG. *Glass*, **18** [4] 102–104, 115 (1941).—S. discusses the manufacture of water glass. See *Ceram. Abs.*, **20** [8] 205 (1941.) B.C.R.

PATENTS

Flexible body. E. A. HAUSER (Research Corp.). U. S. 2,266,638, Dec. 16, 1941 (Feb. 18, 1939).—A flexible, coherent, self-supporting solid body comprising an inert water-insoluble finely divided material incorporated into a coherent and self-supporting flexible matrix of a natural crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought in contact with water to form a plastic hydrogel and exhibiting base-exchange properties, the weight of hydrous oxide being at least equal to the weight of the finely divided material.

Inorganic film products and method of making. E. A. HAUSER (Research Corp.). U. S. 2,266,636, Dec. 16, 1941 (June 7, 1938).—The method which comprises forming a structurally compact film, filament, coating, or the like, of an aqueous suspension of a colloidal, crystalline, inorganic hydrous oxide which contains structural water, is capable of swelling when brought into contact with water to form a plastic hydrogel, and exhibits base-exchange properties and drying it by exposing at least half of the surface area thereof to a drying atmosphere, the film, filament, or coating being coherent, flexible, and self-supporting.

Obtaining chromium oxide. S. E. GERTLER (Harry I. Stein). U. S. 2,263,623, Nov. 25, 1941 (Sept. 11, 1939).—A method of obtaining chromium oxide consisting in passing fumes of an inorganic gas containing chlorine over a granular mass of chromite ore, heated to a combining temperature, to form CrO_2Cl_2 and $FeCl_3$, in a gaseous condition, directing the mixed gases into a chamber in which is maintained a temperature between those of the points of vaporization of the two gases, CrO_2Cl_2 and $FeCl_3$, thus causing condensation of the gaseous $FeCl_3$ while maintaining the CrO_2Cl_2 as a gas, separating the gas from the liquid $FeCl_3$, then causing the temperature of the gaseous CrO_2Cl_2 to be lowered to a point where the CrO_2Cl_2 is condensed as a liquid, and then passing the liquid CrO_2Cl_2 into a receptacle heated to a dull red to release the chlorine therefrom and to cause Cr_2O_3 to be left as a deposit.

Waterproofing and flexibilizing clay films. E. A. HAUSER (Research Corp.). U. S. 2,266,637, Dec. 16, 1941 (Feb. 18, 1939).—The method which comprises forming a coherent, flexible, self-supporting solid body consisting essentially of a crystalline inorganic hydrous oxide having a lattice structure and containing structural water and capable of swelling when brought in contact with water to form a plastic hydrogel and exhibiting base-exchange properties, rendering the solid body insoluble in water by the action of a cation capable of base exchange with the hydrous oxide, and rendering the solid body more flexible by the action of an organic compound capable of entering the lattice structure of the hydrous oxide.

Zirconium oxide manufacture. C. J. KINZIE AND D. S. HAKE (Titanium Alloy Mfg. Co.). Can. 400,512, Nov. 4, 1941 (June 8, 1939). G.M.H.

General

Absenteeism in industry. R. D. MUDD. *Trained Nurse & Hospital Rev.*, **106**, 344–50 (May, 1941).—The problem of absenteeism is fully discussed with reference to (1) general importance, (2) records, (3) distribution, and (4) control. The gravity of the problem is now increasing on account of national defense. M. believes that it is important to record every absence regardless of its length. Each absent employee should be interviewed by a nurse or a doctor prior to his return to work. The records should be complete and should be recorded on a master sheet in addition to individual records so that they can be studied monthly or yearly. Distribution of absences according to a number of factors is discussed fully with the aid of data and charts compiled by W. G. Hazard of the Owens-Illinois Glass Co. The records show that 86.5% of all absences are of less than 8 days' duration, and 71.1% are of less than 4 days. Although short absences comprise a small percentage of the total time lost, they should receive full consideration on account of possible contagion (especially in respiratory affections), turnover, and expense to the

employer. Not more than 1% of absences is due to diseases legally classified as occupational, and absences caused by nonindustrial accidents are 6 to 10 times more frequent than those caused by industrial accidents. Absences increase slightly in frequency with age, but the length of disability increases in a greater ratio. The following factors in control of absenteeism are discussed: (1) amount of checking of absences, (2) occupational exposures, (3) physical examinations, (4) medical and surgical first aid, (5) control by private physicians, (6) control in small industries, and (7) reporting to established agencies. The nurse and the physician can and should exert an influence on lowering absence rates. The more absences are checked, the fewer there will be. Proper supervision of safety and of health hazards leads to greater care at home and elsewhere as well as at work. Physical examination and records associated with first-aid treatment disclose conditions that will guide the private physician in correcting them. The private physician should return the patient to work as soon as he is well. M. believes that insurance for Sunday disabilities should be discontinued, decreasing the number of absences between Thursday and Saturday. Visiting nurse associations for small plants and cooperation with state and national agencies in reporting absences are recommended. F.S.M.

Air dilution in industrial ventilation: III. W. C. L. HEMEON. *Heating & Ventilating*, **38**, 40–42 (Feb., 1941).—H. first considers local exhaust vs. dilution ventilation. In general, where pneumoconiosis-producing dusts, lead fumes and dust, mercury, chlorinated naphthalenes, etc., are present, only local exhaust systems can be used. Exceptions occur in situations of temporary large-scale contamination, as in foundries during the dumping of castings and conditioning of sand, and then only if the processes are of relatively short duration and the volume of ventilation is generous. Air distribution is discussed. In rooms with the same openings, it is immaterial whether a blower, an exhaust fan, or both, with the same capacity, are used. The air entering a room tends to blow in a straight line, and the leaving air currents follow the law of local exhaust hoods, regardless of which method is used. Air entrainment around positive air streams, localized dilution, and objectionable drafts are also considered. F.S.M.

Briggs Mfg. Co. fights occupational diseases. R. G. FRENCH. *Amer. Business*, **11**, 18–19, 48–49 (April, 1941).—F. gives an account of the experience of the Briggs Mfg. Co. in combating occupational disease. In a plant of 20,000 employees, two physicians, two technicians, and one chemist devote their full time to hygiene. All new materials are examined for toxic constituents. Lead dust, mostly from grinding operations, is removed by a push-pull ventilating system, and all of the usual precautions against lead poisoning are observed; a printed employee's handbook contains all rules. Air samples are taken frequently. Special allergies are noted, and analysis for possible sources of dermatitis and a change of occupation for sensitive persons have reduced such trouble to a minimum. The physical-examination program includes watching for communicable diseases and preventing contagion. The program has repaid the company in maintaining health in the city, in promoting steady employment, in contributing to a better product, and in providing insurance against the possibility of occupational diseases. F.S.M.

Clinical evaluation of disability in pulmonary diseases of industry. E. MAYER. *Jour. Amer. Med. Assn.*, **116**, 97–100 (Jan. 11, 1941).—M. presents a discussion on the numerous problems that arise in determining compensability for pulmonary diseases, based on his experience on the New York State Labor Department board of impartial consultants which reviews controversial compensation claims. There are two types of problem: (1) that in which the disease is related to a definite industrial hazard, but it must be decided whether it is disabling; and (2) that in which disability is recognized, but the question is whether the occupation is responsible. M. discusses these problems under the following headings: (1) etiology, (2) production of lung injury and its anatomic results, (3) recognition of pulmonary illnesses, and (4) the manner in which such illnesses produce pulmonary incapacity, particularly with respect to reliable clinical and laboratory procedures for determining such disability. Two cases are described. Three types of pulmonary function tests are cited and discussed in detail: (1) the test for ventilation, or the ability of the lung to inflate and deflate; (2) gas-exchange tests, which measure the oxygen debt, the oxygen deficit, and the oxygen unsaturation of the arterial blood hemoglobin; and (3) measurement of the efficiency of the pulmonary circulation. M. submits the following classification of disability grading: (*a*) phase of compensation, in which pulmonary fibrosis and emphysema are present to a considerable degree, but the emphysema is still compensatory and does not restrict the capacity for moderate exercise; (*b*) latent decompensation, in which fibrosis and emphysema are extensive, with marked restriction of exercise capacity and with dyspnea occurring regularly on moderate exercise; and (*c*) manifest decompensation, where the fibrosis and emphysema are associated with more or less dyspnea even while the patient is at rest. F.S.M.

Determination of lead in air by means of dithizone. V. M. PRIKHNYA. *Zavodskaya Lab.*, **8**, 283–86 (1939).—Modified Palmer tubes containing nitric acid as an absorbing agent were used for the determination of lead in air. Two tubes in parallel and one control tube were used. The control tube contained no lead at an air speed of 10 l. per min. F.S.M.

Fitness in industry. ANON. *Nature*, **146**, 585–86 (Nov. 2, 1940).—The blackout, the seven-day week, and night shifts deprive workers of sunlight. Some English companies are providing artificial sunlight treatments, as fitness in industry is of primary importance and nothing that will contribute to the good health and high morale of industrial workers should be neglected. The care of eyesight and of the feet is also of vital importance. Music in working hours has been found beneficial, care being taken to restrict one class of music to a working session, as changes in tempo upset working rhythm. F.S.M.

Industrial dermatitis. D. C. STRAUS. *Nat. Safety News*, **43**, 36, 82 (Jan., 1941).—In Illinois, during the first two years of operation of the Occupational Disease Act of 1936, 107 claims out of a total of 474, or 22.5%, were for occupational skin diseases. In 1939, the ratio had risen to 39.3%, which was a higher percentage than for any other type of occupational disease. A similar increase has occurred in 5 other states. Sodium hexametaphosphate, applied to the hands and dried before working, proved completely successful in combating dermatitis from washing compounds containing chlorine. "Chemical gloves" or skin coatings insoluble in the solvents being handled are of two types, water soluble and waterproof. The first type gives good protection against paint, lacquers, varnishes, oils, greases, waxes, thinners, carbon black, lead oxides, carbon paper, etc. The second type is used for protection against cutting compounds and cooling lubricants in which the water content exceeds 10% and against strong acid and alkaline solutions. F.S.M.

Industrial health program in Maryland. R. H. FLINN. *Maryland State Dept. Health Monthly Bull.*, No. 13, pp. 30–35 (June, 1941).—F. gives an account of the intensified industrial health activities in Maryland. Practical surveys of about forty industrial plants are being made in cooperation with the county health officers and their staffs. Educational efforts of various kinds are being put into operation. It is emphasized that the successful promotion of an industrial-health program can best be accomplished by the closely combined efforts of the physician, the industrial-hygiene engineer, and the chemist, in collaboration with other state, local, and federal agencies, the accident commission, medical societies, employer and employee groups, universities, and companies interested in industrial casualty insurance. F.S.M.

New materials in the glass and ceramic industries. RUDOLF BARTA. *Chem. Obzor*, **15**, 50–59 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 3240.—B. summarizes the development of the silicate industry and the important varieties and properties of glass, brick, refractory ma-

terials, fine ceramic ware, lime gypsum, MgO cement, cement, and concrete. M.V.C.

Physical fitness. E. Jokl and E. H. Cluver. *Jour. Amer. Med. Assn.*, **116**, 2383–89 (May 24, 1941).—The results of the investigations are a challenge to the conventional methods of determining fitness and employability. Thirty-two young men in South Africa were unable to obtain or retain employment, although they had all received primary education and were free from all diseases which would brand them "unfit" (according to all standards established by labor and recruiting offices and army medical corps). The reasons for their condition were demonstrated by physical-performance tests to be low strength and skill caused by poverty and consequent unsatisfactory diet, bad housing, and poor general standard of living. Their physical condition and failure in work resulted in dullness, bitter mental attitude, and lack of initiative. A special camp was established under the direction of the South African Defense Force for the purpose of training young men suffering from such handicaps. The men underwent a six-month course of training under military discipline, with stress on physical training and drill. Physiological, postural, anthropometric, and physical performance tests, made frequently, showed a rapid rise toward normal levels, and the men's mental attitude likewise improved. Suitable employment at normal wages was provided for 90% of the men thus trained, and an analysis of pay sheets for a sample group of these workers for four years showed that they had achieved full economic rehabilitation. The authors also conducted an extensive study of the growth in physical efficiency of a group of children between 5 and 20 years of age, including English, Afrikander, Jewish, Bantu, Cape Colored, Indian, and Chinese. The similarity between the standards of physiologic performance of the different racial groups was striking. The effect of puberty on the growth of physical efficiency is noteworthy. It is desirable to collect more evidence on the relationship between subclinical nutritional deficiencies and physical efficiency. The terms "fitness" and "efficiency," generally very loosely applied, should be considered with the question, "Fitness and efficiency for what?" To illustrate this point, the authors cite instances of remarkable athletic ability in specialized fields in persons with severe physical defects, some evident at once and others discovered only after death. They believe that the only satisfactory measure of fitness for employment is physical performance and predict that theories and concepts of physical fitness will change when more physiologic and clinical experiences in this field are presented in the medical literature. F.S.M.

Sand producers discuss silicosis. Anon. *Stone*, **51**, 270 (July, 1940).—The discussions at the June, 1940, meeting of the National Industrial Sand Assn. at White Sulphur Springs, W. Va., are reported. The value of medical control in industry was shown, but it was stated that social incompetence must not be overlooked as the principal cause of rejections of workers along with physical disqualifications. Silicosis was discussed in detail, and the legal aspects of current developments in industrial hygiene were presented. Pre-employment and periodic examinations may avoid or limit the employer's legal liability for industrial injuries sustained by employees engaged in hazardous occupations. While the employer has the legal right to request the prospective employee to subject himself to physical examination, he cannot compel him to submit to periodic examination after he is employed. This can be done only by agreement. The New York industrial codes setting up permissible limits for dust concentrations for certain industries were also discussed. F.S.M.

Side lights on history of psychrometry. David Dropkin. *Mech. Eng.*, **63** [5] 369–70, 376 (1941).—Illustrated. F.G.H.

Dust units employed in ventilation. F. F. Kravath. *Penna. Dept. Labor & Ind., Safe Practice Bull.*, No. 63 (May, 1941).—K. reviews the general types of filters and their capabilities, failings, and comparative worth as shown by the experience record of installations in the abrasive industry. The types discussed include the gravitational filter or settling tank, the cyclone filter, cloth filters, electrical precipitation, and air washers. The gravitational filter is recommended only as a preliminary cleaning device. Its velocities should be kept at 100 to 250 ft. per min. This type of installation is practically wear and maintenance free, as the dust comes in contact with almost none of the filter parts while it still has any velocity. The cyclone filter, unlike the gravitational filter, increases in efficiency with decrease in the diameter. Because of its high efficiencies, it is probably the most widely used collector. These installations find their greatest application where the dust or collected material is nonabrasive in action. Cloth filters are used primarily where high efficiencies are necessary for the reclamation of valuable material, where recirculation is desired as a means of reducing heating losses, or in residential districts where it is unlawful to discharge visible solids into the atmosphere. The original cost of the cloth filter is higher than that of the cyclone, but its efficiency is unquestioned, its life is extremely long, and maintenance is fairly simple. Electrical precipitation offers perhaps the most efficient type of separation, but its initial cost is high. Its application will therefore probably be restricted to the reclamation of valuable or extremely dangerous materials. The efficiencies of air washers are somewhat lower than those of cloth filters, but, occasionally, improper application and maintenance of cloth filters tend to make the air washer the more practical unit. Its cost averages about one third that of the cloth filter. F.S.M.

Effect of therapeutic agents in the treatment of lead poisoning. F. L. Smith, II. *Penna. Dept. Labor & Ind., Safe Practice Bull.*, No. 52, Part III, 13 pp. (June, 1941).—Lead determinations were made on the whole blood, serum, and cells and fibrin of a number of healthy persons, patients with disorders other than plumbism, and patients with latent plumbism. In nonleaded persons, there was no lead in the serum, a maximum of 0.013 mgm. per 10 gm. in the cells and fibrin, and a maximum of 0.006 mgm. per 10 gm. in the whole blood. The 92 cases of latent plumbism always showed 0.001 to 0.004 mgm. of lead per 10 gm. of serum, but in 43 of the 92 cases the whole blood and cell and fibrin contents were within the normal range; symptoms of lead poisoning were absent but could be produced by acid therapy. These results are in sharp contrast to those reported recently, in which it was claimed that abnormal quantities of lead could be present in the blood without indicating lead poisoning. Therapeutic measures are of two distinct classes, according to the result desired: elimination or storage. The choice must be made for each case. Where the elimination of lead is massive, inactivation by storage or tissue absorption is indicated. The treatment involves no hospitalization, but the possibility of development into an active case always remains. In chronic lead poisoning, controlled deleading should be used during an inactive phase without allowing the occurrence of acute lead intoxication. Lists of therapeutic agents for producing elimination and storage are given, and clinical reports on the effects of most of the agents are presented in detail. For elimination, phosphoric acid appears to be most successful. Results with magnesium sulfate were adverse; it should never be used in lead poisoning cases. Vitamin B had no effect. Storage is most successfully accomplished by administration of ascorbic acid. The procedure adopted by S., as indicated by the experimental results, includes (1) deleading with acid; (2) stopping too rapid a liberation of lead with ascorbic acid, ferrous ascorbate, or calcium gluconate and vitamin D; (3) resting the patient on ascorbic acid therapy; and (4) repeating the process until a normal blood-lead picture is obtained which does not change on (5) the administration of phosphoric or hydrochloric acids. F.S.M.

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